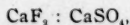


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THE CALCULATION OF ATOMIC WEIGHTS.

BY F. W. CLARKE.

In the ordinary discussion of ratios relative to atomic weights, different results may be obtained by varying the method of computation. This is due to the fact that the ratios as measured are not absolute, but subject to errors, which should be, but are not usually, distributed. In most cases the tendency is to accumulate all errors, accidental or systematic, upon the constant which is last determined, a procedure which is obviously unscientific. Take, for example, the ratio



upon which our knowledge of the atomic weight of fluorine chiefly depends. In the actual measurement certain errors of observation occur; the data are reduced with assumed values for the atomic weights of calcium, sulphur, and oxygen, which are themselves, to a greater or less extent, inexact, and all of these inaccuracies are brought together in the final result of calculation. If oxygen be taken as the standard of atomic weights, and therefore not subject to error, the atomic weight of fluorine will contain the error of the experiment,

plus the errors in the atomic weights of calcium and sulphur ; and whether these compensate one another or not we have no means of knowing. Moreover, each error exerts its maximum effect, whose extent can hardly be estimated.

It is generally agreed, with but few dissenting voices, that the work of Stas upon some of the more fundamental atomic weights, is as accurate as the present resources of experimental chemistry can make it. And yet, even here, discrepancies exist which the ordinary method of calculation fails to reconcile. The ratios measured by Stas have been discussed by various writers, especially by Stas himself, by Ostwald, by Thomsen, and by Van der Plaats, and the results of the several computations vary with the method of calculation. Van der Plaats,¹ in particular, has illustrated this fact by making two calculations, giving the ratios equal weight in one (A), and weight inversely proportional to the squares of their probable errors in the other (B). In the following table the various results of the reductions appear :

	Stas.	Ostwald.	Thomsen.	Van der Plaats (A).	Van der Plaats (B).
Ag	107.930	107.9376	107.9299	107.9202	107.9244
Cl	35.457	35.4529	35.4494	35.4516	35.4565
Br	79.952	79.9628	79.9510	79.9407	79.9548
I	126.850	126.8640	126.8556	126.8445	126.8494
Na	23.043	23.0575	23.0543	23.0453	23.0443
K	39.137	39.1361	39.1507	39.1414	39.1403
N	14.044	14.0410	14.0396	14.0421	14.0519
S	32.074	32.0626	32.0606	32.0576	32.0590
Li	7.022	7.0303	7.0307	7.0273	7.0235
Pb	206.926	206.911	206.9042	206.9089	206.9308

The differences thus shown are slight, but in the case of bromine they amount to more than two in the second decimal place, an uncertainty greater than is commonly recognized. It is an uncertainty which affects all other determinations depending upon the atomic weight of bromine as an antecedent factor, and which ought to be appreciably diminished. With sulphur and nitrogen the divergencies are proportionately even greater.

Now, bearing in mind that the so-called determination of

¹ Compt. rend., 116, 1362.

atomic weights is nothing more than the accurate measurement of chemical ratios, let us consider how the latter are to be treated. In the case first cited, the ratio between calcium fluoride and calcium sulphate, the usual method of calculation, is evidently defective, and yet, with existing data, it is the only practicable mode of procedure. With adequate data the ratio should contribute to our knowledge of at least three atomic weights, those of fluorine, calcium, and sulphur, its errors of observation being divided into three parts and not concentrated upon a single factor. That is, the ratio should be combined with other ratios in such a manner that several atomic weights might be simultaneously computed, all errors being so distributed as to reduce their influence to a minimum. With some groups of ratios calculations of this sort are already possible, and Van der Plaats' reduction of Stas' determinations is a good illustration of my meaning. In this case 23 ratios, involving the atomic weights of 10 elements, were combined into one group of normal equations, and the latter were then solved once for all. The method followed was the well-known method of least squares, and that is the only process which satisfies all conditions. Given enough data of sufficient accuracy, and the method of least squares is applicable to the problem in question, with insufficient evidence or doubtful measurements no solution is satisfactory. The mathematical operations are well understood; it is for the chemist to furnish suitable material to which they may be applied.

In order to illustrate more fully the foregoing considerations, I have combined 30 ratios, involving the atomic weights of silver, chlorine, bromine, iodine, nitrogen, sodium, and potassium, into 7 normal equations, in which the constants named appear as the unknown quantities. The ratios are given on pages 53 and 70 of my "*Recalculation of the Atomic Weights*,"¹ and contain, in addition to the work of Stas, determinations by Berzelius, Penny, Pelouze, Marignac, Dumas, Gerhardt, Maumené, Turner, Millon, Huntington, Richards, Ramsay and Aston, Hardin, Thomsen, and Hibbs. In short,

¹ Smithsonian "Constants of Nature," Part V., 1897.

all determinations of the ratios in question, made up to 1897, are included in the discussion, in order that the effect of such a combination may distinctly appear. The basis of calculation, the standards of reference, are $O = 16$ and $H = 1.0079$, these values being taken as known. Personally, I prefer the hydrogen unit as a starting point, but in the present case the results are to be compared with those of other computers, as previously cited.

To show the method of calculation, let me first take one or two ratios separately. For instance, the ratio

$$\text{Ag} : \text{Br} :: 100 : 74.080$$

may be written $100 \text{ Br} = 74.080 \text{ Ag}$, when the symbols Br and Ag represent the two atomic weights respectively. So, also, the ratio

$$\text{KClO}_3 : \text{O}_3 :: 100 : 39.154$$

becomes in linear form

$$39.154 \text{ K} + 39.154 \text{ Cl} = 2920.608.$$

From 30 equations of this kind the 7 normals are constructed, each ratio contributing toward the establishment of each atomic weight represented in it. In this way errors of measurement are divided up and distributed, and even systematic errors find their influence diminished.

If all of the 30 ratios were equal in value and importance, the formation of the normals would be a comparatively simple matter, but such is not the case. Some are very exact, others are more than doubtful, and weight must be assigned accordingly. The rigorous rule is to give each measurement weight inversely proportional to the square of its probable error, and as the latter is given in every case, the rule has been applied. Only, instead of multiplying each equation by its weight, which would give coefficients of excessive size, I have divided them by suitable factors and so reduced the coefficients to manageable dimensions. The principle is unchanged, but its mode of application is somewhat unusual. The same result, however, is reached in the end, and the element of personal judgment is entirely eliminated from the discussion. Each

ratio weights itself, regardless of any preferences upon my part.

Now, taking the regular method of least squares, the 30 equations, after weighting, reduce to the following normals, seven equations containing the seven unknown quantities:

- (1) $+5251.3245 \text{ Ag} - 6726.5755 \text{ Cl} - 599.0278 \text{ Br} - 143.1342 \text{ I}$
 $-1238.429 \text{ N} - 1871.5887 \text{ Na} - 4417.7167 \text{ K} = 28800.227$
- (2) $-6726.5755 \text{ Ag} + 12014.6535 \text{ Cl} - 24.7694 \text{ Br} - 2.8347 \text{ I}$
 $+471.803 \text{ N} + 3146.9379 \text{ Na} + 6758.0443 \text{ K} = 41302.978$
- (3) $-599.0278 \text{ Ag} - 24.7694 \text{ Cl} + 716.8553 \text{ Br} + 156.250 \text{ N}$
 $+204.082 \text{ Na} + 27.72 \text{ K} = -230.712$
- (4) $-143.1342 \text{ Ag} - 2.8347 \text{ Cl} + 129.2642 \text{ I} + 0.5536 \text{ K} =$
 868.704
- (5) $-1238.429 \text{ Ag} + 471.803 \text{ Cl} + 156.250 \text{ Br} + 2954.376 \text{ N}$
 $-35.1434 \text{ Na} - 334.7707 \text{ K} = -76872.85$
- (6) $-1871.5887 \text{ Ag} + 3146.9379 \text{ Cl} + 204.082 \text{ Br} - 35.1434 \text{ N}$
 $+3319.6292 \text{ Na} = 1919.906$
- (7) $-4417.7167 \text{ Ag} + 6758.0443 \text{ Cl} + 27.72 \text{ Br} + 0.5536 \text{ I}$
 $-334.7707 \text{ N} + 6748.573 \text{ K} = 24505.141$

A glance at these equations is enough to indicate some of their deficiencies. The first two only are complete; in the others eight terms are missing. In the fourth equation, which represents iodine, the terms corresponding to sodium, bromine, and nitrogen are absent, and even potassium is represented by a coefficient which is ridiculously small. Many other coefficients are smaller than they should be, and this indicates the inadequacy of some of the data. To be really satisfactory, no one of the 49 coefficients should be wanting, and all should be reasonably large. Moreover, every coefficient should represent data drawn from more than one ratio, and in too many instances this is not the case. Were Stas' data alone considered, the normals would be still more incomplete, even though the outcome of the solution might be considered better.

Upon solving the 7 normal equations the following values are obtained:

Ag 107.9525			
Cl	35.4521	N	14.0527
Br	79.9687	Na	23.0636
I	126.8663	K	39.1573

These, except in the case of chlorine, are considerably higher than any of the values given in the table of reductions derived from the work of Stas, and yet they are not so inconsistent with the latter as they might appear to be at first sight. From the new atomic weights we can compute the value of each one of Stas' ratios, and so compare the result with the measurements which he actually made. This is done in the following table, which gives in each case the lowest and highest determination by the great Belgian.

Ratio.	Stas.		Calculated.
	Lowest.	Highest.	
KClO ₃ : O ₃	39.1527	39.162	39.149
AgClO ₃ : O ₃	25.078	25.081	25.078
AgBrO ₃ : O ₃	20.349	20.351	20.346
AgIO ₃ : O ₃	16.972	16.9761	16.972
Ag : Cl	32.841	32.849	32.840
Ag : Br	74.079	74.083	74.078
Ag : I	117.529	117.543	117.520
Ag : KCl	69.099 ¹	69.1249	69.114
Ag : KBr	110.332	110.361	110.354
Ag : NaCl	54.2054	54.2093	54.205
Ag : NaBr	95.4383	95.4426	95.440
Ag : NH ₄ Cl	49.592	49.602	49.592
Ag : NH ₄ Br	90.823	90.8317	90.830
Ag : AgNO ₃	157.463	157.510	157.481
AgNO ₃ : KCl	43.864	43.885	43.886
KCl : KNO ₃	135.638	135.655	135.654
NaCl : NaNO ₃	145.443	145.469	145.458

In ten cases out of the seventeen the calculated ratios fall within the limits of variation shown by the experiments of Stas; in six cases they are lower than his lowest, and in only one case is the result too high. In no case is the divergence large, and in most instances it is remarkably small. My conclusion from all of these considerations is, that although the new figures should not replace the accepted values for the several atomic weights, they are not to be lightly disregarded. They serve to exemplify the ultimate method of calculation, and to show that the data need reinforcement by additional determinations, which should complete the normals

¹ Early work, supplanted by later and better measurements.

and raise the weak coefficients to adequate magnitude. When that is done, when, say 50 ratios are available instead of 30, then will the method of least squares be fully applicable to the problem, and its use will give the most probable results. To this end, ratios based upon analyses of sodium bromate, iodate and iodide, potassium bromate and iodate, and ammonium iodide, are especially desirable. Other ratios connecting chlorine, bromine, and iodine with one another are also much needed and should not be difficult to determine. For example, the ratio $\text{AgClO}_3 : \text{AgBr}$ ought to be easy of measurement, and also the reverse ratio $\text{AgBrO}_3 : \text{AgCl}$.

If the oxygen-hydrogen ratio be considered the base line in our system of atomic weights, then the determination of the 7 constants now under consideration might be compared to a primary triangulation. For this purpose no accuracy is too high, no refinement of details too laborious. If the atomic weights of carbon and sulphur should be included in the scheme, giving 9 normal equations for solution, the range of possibilities would be much increased and the results of the discussion could be made more satisfactory. With existing data, 44 ratios, good and bad, are now available, and their distribution in the normals can be seen in the following table. Here each horizontal line represents the left-hand side of one equation, and each figure indicates the number of ratios which would influence a given coefficient :

	Ag.	Cl.	Br.	I.	N.	Na.	K.	C.	S.
Ag	31	14	6	4	7	3	5	7	3
Cl	14	20	1	1	9	5	6	—	1
Br	6	1	7	—	1	1	2	—	—
I	4	1	—	5	—	—	2	—	—
N	7	9	1	—	13	2	3	1	—
Na	3	5	1	—	2	7	—	1	1
K	5	6	2	2	3	—	10	—	—
C	7	—	—	—	1	1	—	11	1
S	3	1	—	—	—	1	—	1	4

That is, the normal for silver would be formed from 31 ratios containing silver, 14 containing chlorine, etc. The other equations would all be incomplete, 24 terms being absent, and 18 more being affected only by single ratios. To

supply the 24 and to improve the 18 is the experimental part of the problem, and this is not so great a task as it might seem to be at a first glance. For example, suppose that the ratio $\text{AgCNS} : \text{AgI}$ were capable of measurement. Its errors of observation would be divided between 5 elements, 8 missing coefficients would be supplied, and 25 coefficients in all would be affected. Merely to fill the gaps in the equations, therefore, is easy; to fill them properly is a more weighty question. To this end, 40 or 50 new ratios ought to be carefully determined, giving a system of ratios containing from 80 to 100 in all. For one chemist so great a labor would be hardly possible, but by cooperation between several workers the task might be performed, and in something like reasonable time. The methods of manipulation, the precautions to be observed, the difficulties to be encountered, are all well known, and that consideration helps to simplify the problem. Stas and Marignac have laid the foundations, and with their recorded experience to guide us we should be able to build the structure higher without excessive difficulty.

RESEARCHES ON THE OXIDES OF TUNGSTEN.

BY E. T. ALLEN AND V. H. GOTTSCHALK.

Of all the different oxides of tungsten which have been described only two, WO_2 and WO_3 , are of established composition. Formulas for at least half a dozen others have been proposed. Thus, Malaguti prepared a blue substance to which he assigned the formula W_2O_8 , by heating tungstic oxide in dry hydrogen by means of an alcohol lamp.¹ Von Ulsar asserted that the compound obtained by heating tungstic trioxide strongly in hydrogen was W_3O_8 . Gmelin obtained a blue compound by reducing tungstic trioxide in a current of carbon monoxide, to which Von Ulsar assigned the formula W_4O_{11} ,² though Desi was unable to get a homogeneous product in this way.³

By oxidizing metallic tungsten with strong sulphuric acid

¹ Ann. chim. phys., [2], 60, 272 (1835).

² Graham-Otto: "Lehrbuch der Chemie," Vol. II., p. 1161.

³ J. Am. Chem. Soc., 19, 230.

under various conditions, Desi¹ obtained several substances which he considered chemical individuals having the formulas WO , W_2O_3 , W_3O_5 , and W_5O_9 . These substances, like all the oxides previously referred to, were blue or bluish in color.

It was in the hope of clearing up some of these uncertainties that the present investigation was undertaken. None of the products under consideration can be sublimed or otherwise purified, consequently there is danger of being misled by mixtures. The rapid oxidation to which those which are prepared by wet methods are subject, constitutes another difficulty in their investigation. Finally, so far as known, none of them forms salts; therefore, the formulas have to be deduced from analysis. And, since the ratio between tungsten and oxygen is large (184 : 16), the difference in the percentage of the elements demanded by such compounds as W_mO_n and $W_{m+1}O_{n+3}$ is correspondingly small. We have overcome these difficulties, in part, by using pure materials, washing the products out of contact with air, analyzing them without drying, and using pretty large portions for analysis. Such mixtures as result from incomplete reactions we have avoided by treating our products with successive portions of reagent.

In establishing our formulas we have also been aided by certain theoretical considerations. Thus far we have experimented only on the action which reducing agents exert on tungstic acid. This compound is much more difficult to reduce than chromic or molybdic acid.² In alkaline (tungstate) solution it may be boiled with grape sugar, hydroxylamine,³ or even metallic aluminum, without undergoing any reduction. Suspended in hot concentrated hydrochloric acid, it is stable toward hydroxylamine, oxalic acid, or alcohol. Even in sealed tubes, at 200° C., the last-named reagent effected no change in the appearance of the tungstic acid, but yielded only ethyl chloride. A solution of sulphurous acid, saturated at a low temperature, may be heated to 200° C. in

¹ J. Am. Chem. Soc., 19, 213.

² Regarding the reduction of tungstic acid in the dry way, see Ehrenfeldt: J. Am. Chem. Soc., 17, 381.

³ Hydroxylamine forms a compound to be described later.

sealed tubes, with tungstic acid, without reducing more than traces in the upper surface layer.¹

Nascent hydrogen, liberated from acids by the action of metals, reduces it, but since the final product seems to be metallic tungsten, this reagent did not seem to promise well for the preparation of a pure oxide. In stannous chloride and hydriodic acid, however, we found reagents well adapted to our purpose.

Reduction of Tungstic Acid with Stannous Chloride.

Stannous chloride reduces tungstic acid to a fine, dark-blue, insoluble substance. The tungstic acid merely requires to be heated on the water-bath with an excess of acidified stannous chloride solution until the color indicates that the change is complete. In our earlier experiments we poured off the reagent at this stage and repeated the reduction, but analyses of the substance showed that this was unnecessary. Three or four grams of tungstic acid is easily reduced by 20 to 25 cc. of stannous chloride solution, which may be prepared by dissolving 8 grams tin in 25 cc. concentrated hydrochloric acid. A 100 cc. Erlenmeyer flask, closed by a one-hole stopper provided with a Bunsen valve, is a convenient reaction vessel, since it serves to keep the substances out of contact with air. The product must be washed in hydrogen or carbon dioxide. A cylinder was made by cutting off the lower third of a wide-mouthed bottle, about $2\frac{1}{2}$ inches in diameter, and grinding down the edge. The smaller end was closed by a perforated stopper, through which passed the stem of the funnel which was enclosed by the cylinder. Through a second hole in this stopper passed the conducting tube for carbon dioxide (hydrogen, if used, should of course be introduced at the top). The top of the cylinder was closed by a one-hole stopper, which supported a small dropping-funnel.² To prevent any diffusion of air into the apparatus, the stem of the funnel on which the filtration was made, dipped

¹ J. Am. Chem. Soc., 19, 223-226. It is evident that Desi misinterpreted the separation of sulphur here, since sulphurous acid alone gives the same result.

² This apparatus is similar to that described by H. N. Stokes, Bull. U. S. Geol. Surv. 186.

under water. When an experiment was to be carried out carbon dioxide, which first passed over a long train of red hot copper, was allowed to flow through the apparatus for an hour or more, until the air was removed both from the cylinder and the dropping funnel. The stannous chloride was then quickly decanted from the blue compound, which was then rapidly washed through the dropping funnel by air-free water. The operation requires but a few minutes, during which the substance is wet by the reducing agent. The washing was done at first by air-free water, acidified by hydrochloric acid, and finally by water alone. We, at first, used alcohol and ether to complete the washing, but alcohol absorbs oxygen from the air to a far greater degree than water, and, consequently, had to be discarded. Our earlier preparations were dried in the washing apparatus, or in a vacuum desiccator, which we filled with carbonic acid before exhausting, but despite our utmost pains there were usually signs of oxidation, so that we at last gave up drying entirely and determined the ratio of oxygen absorbed to the tungsten contained in the substance. We insert several analyses of the dried product which were nearly pure, since water is an essential constituent. These were made by heating weighed quantities, noting the losses, and collecting the water. The difference between the total loss and the water found is the quantity of oxygen absorbed from the air.

Table I.—Analyses of Blue Hydroxide (Dry).

	Found.					Aver- age.	Calcu- lated for W ₅ O ₁₄ H ₂ O.
	I.	II.	III.	IV.	V.		
Time of dry- ing (hours)	14	18	1.5	1.75	1.5		
Weight taken	2.8386	2.8396	3.0575	1.8038	2.7883		
Loss on heat'g	0.0172	0.0188	0.0199	0.0137	0.0173		
P'c'tage loss	0.60	0.66	0.65	0.76	0.62		
Water found	0.0509	0.0514	0.0520	0.0323	0.0452		
P'c't'ge water	1.79	1.81	1.70	1.79	1.62	1.74	1.55
Percentage O absorbed	1.19	1.15	1.05	1.03	1.00	1.08	1.37
O calc. as per cent anhyd. substance	1.21	1.16	1.07	1.05	1.01	1.10	

The analyses in Table II. were made as follows: As soon as the tin was completely washed out of the blue compound the latter was rapidly transferred from the filter into a measured excess of titrated chromic acid, by means of a wash-bottle filled with air-free water. The mixture was then boiled for about fifteen minutes, or until complete oxidation was accomplished. After cooling, the excess of chromic acid was titrated by ferrous sulphate in the usual way. The tungstic acid does not interfere, and the loss of the same by dipping out is negligible, since a loss of 20 milligrams when 3 grams substance is used, occasions an error of only 0.01 per cent in the oxygen absorbed. After the titration, the tungstic acid is filtered, washed with dilute hydrochloric acid, and burned in a platinum crucible to a constant weight. As soon as the filter is charred, the cover of the crucible is removed. The blast should not be used.

Table II.—Analysis of Blue Hydroxide (Wet).

	I.	II. Found.	III.	IV.	Average.	Calculated for W_5O_{14} .
$K_2Cr_2O_7$ taken (cc.)	50	54.6	50.2	50		
$FeSO_4$ used, in terms of $K_2Cr_2O_7$ (cc.)	29.2	14.8	15.7	16.4		
Available oxygen in $K_2Cr_2O_7$ required in oxidation	0.0209	0.0399	0.0346	0.0336		
WO_3 found	1.5871	3.1092	2.3063	2.7073		
Blue oxide, anhydrous, calculated from $WO_3 - O$	1.5662	3.0693	2.2717	2.6737		
Percent of oxygen absorbed by blue oxide	1.33	1.30	1.52	1.27	1.35	1.39

Reduction of Tungstic Acid by Hydriodic Acid.

In these experiments the tungstic acid was heated with the reagent in sealed tubes at about 200° C. About 1.5 grams WO_3 was used to about 10 cc. of fuming hydriodic acid

(about 1.7 sp. gr.), and the heating was ordinarily continued several hours. We obtained in this way the same indigo-blue substance which we got with stannous chloride, nor did repeated treatment with the reducing agent appear to exercise any influence on the final product. Weak acid did not give a complete reduction, and very concentrated reagent in large excess gave, in one instance, a mixture containing, besides the blue oxide, a black substance which seemed to contain considerable iodide. It was not investigated. All the preparations made with hydriodic acid were analyzed according to the method described on page 331, and a comparison of the results will show that they agree closely with those of Table I.

Table III.—Analysis of Blue Hydroxide Prepared with Hydriodic Acid.

	I.	Found. II.	III. Drying in hydrogen, about 1 hour, at 100°.	Aver- age.	Calculated for $W_2O_4 \cdot$ H_2O .
	Drying in hydrogen, 1-2 hours, at about 60°.	Drying in hydrogen, 1-2 hours, at about 60°.			
Portion I.	0.2528	1.1714	1.0550		
Loss on heating	0.0015	0.0083	0.0031		
Percentage loss	0.59	0.71	0.30		
Portion II.	0.7933	1.0432			
Water found	0.0135	0.0168	0.0152		
Percentage water	1.70	1.61	1.44	1.58	1.55
Per cent oxygen absorbed	1.11	0.90	1.14	1.05	1.37

Properties of the Blue Hydroxide of Tungsten.

This compound is a deep-blue powder, a little brighter than indigo, and purplish in reflected light. It is insoluble in water containing a little hydrochloric acid, while in pure water it may assume a very fine state of division, apparently forming a colloidal solution as tungstic acid does. The blue hydroxide of molybdenum, recently investigated by Guichard,¹ shows this property to a degree far more marked.

The tungsten compound oxidizes in the air, especially when moist, and if heated changes to tungstic trioxide almost in-

¹ Ann. chim. phys., [7], 23, 519.

stantly. Bleaching-powder, hydrogen peroxide, permanganic acid, and chromic acid all oxidize it, but not very rapidly in the cold. Hot concentrated sulphuric acid oxidizes it slowly, and concentrated nitric acid rapidly. Concentrated hydrochloric acid has no effect on it. Strong, cold, caustic alkali solutions, if they change it at all, do so very slowly. Heated, they form alkaline tungstate and evolve a gas. 11.5 cc. of this gas was diluted with air and passed over palladium asbestos. The latter glowed brilliantly. The total condensation was 16 cc., which indicated 10.7 cc. hydrogen. Ammonia also reacts with this compound. Ammonium tungstate passes into solution and a very considerable brown residue remains. No gas is evolved. Ammoniacal silver solution is reduced by it.

It is this blue substance which is formed in the well-known test for tungsten by nascent hydrogen. But nascent hydrogen causes a further reduction to WO_3 , and finally to the metal, so that it would be more rational to employ a little strong stannous chloride instead. As this test is ordinarily performed, one may overlook a very little tungsten, because with tin or zinc and acid the blue color is transitory.

The Bronze Hydroxide of Tungsten.

When the blue hydroxide which has just been described is warmed with concentrated ammonia, a part of the tungsten goes into solution as ammonium tungstate, and there forms, as above stated, a residue which looks brown and only slightly lustrous while covered by the solution, but when washed and dried it appears deep-purple, with a fine bronze luster in reflected light.

Preparation.—The blue oxide, prepared as described previously, is washed quickly into the flask which served in the formation of the blue compound, by a jet of strong ammonia water. The flask is then filled nearly full of ammonia and corked with the Bunsen valve. It should then be gently warmed and put aside to settle. Now the liquid is removed and the treatment repeated. To do this without allowing the

oxide to come in contact with air, let a current of hydrogen slowly force out the liquid through a small syphon, the gas meanwhile replacing the liquid. By a very simple device the same gas current may be made to force in a second portion of ammonia. When 75 cc. of ammonia are used as a portion, the ammonium tungstate may be almost all removed by twice repeating the process. Then fill the flask with boiled water and transfer quickly to the washing apparatus. When the liquid has run through the filter, wash twice with boiled water acidified with sulphuric acid. The analyses of this compound were carried out exactly as described with the blue hydroxide.

Table IV.—Analysis of Bronze Hydroxide (Moist).

	I.	II.	Found. [•] III.	IV.	Aver- age.	Calcu- lated for W ₂ O ₅ .
K ₂ Cr ₂ O ₇ taken (cc.)	45.3	80.1	79.7	76		
FeSO ₄ used, in terms of K ₂ Cr ₂ O ₇ (cc.)	39.1	64.8	58.0	56.1		
K ₂ Cr ₂ O ₇ used in oxi- dation (cc.)	6.2	15.3	21.7	19.9		
Available oxygen in K ₂ Cr ₂ O ₇ used up	0.062	0.0153	0.0217	0.0199		
WO ₃ found	0.2593	0.6662	1.0006	0.8263		
Bronzeoxide, anhy- drous, calculated from WO ₃ — O	0.2531	0.6509	0.9789	0.8064		
Per cent of oxygen absorbed by the bronze oxide	2.45	2.35	2.22	2.47	2.37	2.35

The three following preparations were made under conditions similar to those described above. As they were made earlier in point of time, pains were taken to prove that no more tungsten was extracted by ammonia before any acid was added. They were then washed with hydrochloric acid and dried in a vacuum desiccator. The method of analysis was that described on page 331.

Table V.

	I.	Found. II.	III.	Average.	Calculated for		
					W_2O_5 H_2O .	W_4O_{11} H_2O .	W_6O_{17} H_2O .
Time of drying (hours)	1.5	2.5	3.5				
Weight taken (gram)	0.5440	0.6940	0.6682				
Loss on heating	0.0068	0.0076	0.0058				
Percentage loss	1.25	1.09	0.87				
Water collected	0.0164	0.0202	0.0180				
Per cent water	3.02	2.91	2.69	2.87	2.57	1.93	3.85
Oxygen abs'b'd	1.77	1.82	1.82	1.80 ¹	2.29	1.72	3.42
Oxygen in an- hydrous sub- stance (per cent)	1.82	1.87	1.87	1.85			

Properties.—In color this compound appears purple, with a fine bronze luster in reflected light. In the dry state it is very beautiful. Its chemical properties are similar to those of the blue hydroxide. It is oxidized by the same reagents, but more readily. It changes first to the blue compound and then to the yellow tungstic acid. It is insoluble in hydrochloric acid, but seems to go into solution somewhat in pure water, like the blue oxide and tungstic acid. Hot caustic alkalis form alkaline tungstate and hydrogen. Desi obtained an anhydrous substance, which analyses indicated to be W_2O_5 , by heating ammonium metatungstate, $(NH_4)_6W_6O_{17}$, in closed vessels to a bright redness. He describes it as "a beautiful purple substance with a yellow metallic reflex, insoluble in water, acids, and alkalis."²

It is interesting to compare the action of ammonia on the blue oxide, with the results which Desi obtained with those oxides which he prepared by oxidizing metallic tungsten with strong sulphuric acid. All of them, according to him, give metallic tungsten, when treated with strong ammonia. Now, concentrated sulphuric acid oxidizes the blue compound prepared by us to tungstic acid, and it may perhaps be possible

¹ The low results are readily explained by oxidation. It will be noted that the figures are all higher than W_4O_{11} demands, in spite of oxidation.

² J. Am. Chem. Soc., 19, 227.

that Desi's products were mixtures containing unchanged metal.

In addition to the evidence already presented for the two formulas, $W_5O_{14} \cdot H_2O$ and $W_5O_8 \cdot H_2O$, we may instance the fact that Guichard, who has recently investigated the blue oxide of molybdenum, prepared and analyzed by methods differing from ours, concludes that the true formula for the same is $Mo_5O_{14} \cdot 6H_2O$. The properties of this substance resemble those of $W_5O_{14} \cdot H_2O$. It is, however, completely soluble in pure water, though not in dilute hydrochloric acid, and soluble also in concentrated hydrochloric acid. The result is a green solution, which, according to Guichard, contains $MoCl_4$. Such a green solution is, in fact, obtained when dilute solutions of a molybdate are treated with stannous chloride, while from a tungstate one gets the blue oxide. $W_5O_{14} \cdot H_2O$ differs from $Mo_5O_{14} \cdot 6H_2O$ also in its behavior with ammonia, the latter giving MoO_3 .

$W_5O_8 \cdot H_2O$ finds its analogue among the oxides of uranium. The latter, in its hydrous state, is described as a dark-green powder, but another form appears to exist, closely resembling in appearance the tungsten compound. Berzelius sometimes obtained a purple-brown precipitate, by precipitating with ammonia, a solution of U_5O_8 in acids, and Ebelmen says that when light decomposes uranyl oxalate a hydrated form of U_5O_8 separates in violet-brown flakes.¹

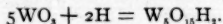
Very recently, Hallopeau has revised the work on the tungsten bronzes.² There are two series of these interesting compounds. The first is prepared by reducing the tungstates at a red heat in dry hydrogen. They possess the general formula $W_5O_8 \cdot M_2O$, where $M = Na$ or K . These bodies possess a metallic luster, and the potassium compound is described as a violet-red substance with a copper reflex, recalling $W_5O_8 \cdot H_2O$ in a striking way. The members of the second series (with exception of the barium compound) are made by reducing the molten tungstates with metallic tin. They possess the general formula $W_5O_{14} \cdot M_2O$, where $M = Na, K, Li$, or

¹ Gmelin-Kraut: *Handbuch der Chemie*, 2, 382.

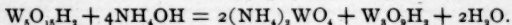
² *Ann. chim. phys.*, [7], 19, 106 (1900).

$\frac{1}{2}$ Ba, and are all dark-blue in color like $W_5O_{14} \cdot H_2O$. So far as composition goes, then, the two compounds described in this paper are the mother-substances of the tungsten bronzes, though it remains to be proved that the connection can be experimentally made.

Assuming our formulas to be correct, the reduction of tungstic trioxide by stannous chloride and hydrochloric acid, or by hydriodic acid, consists in the addition of hydrogen :

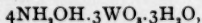


The study of colloidal tungstic acid indicates a molecule much more complex than WO_3 , and other facts are in harmony with this. It is easy to represent such a molecule by a ring structure according with the valence hypothesis, and ring structures usually go with chemical stability. Tungstic acid at any rate shows a much greater stability than its chromium and molybdenum analogues, and it is not impossible that in the above reduction a single complex molecule is reduced like many organic compounds where oxygen becomes hydroxyl. The action of ammonia on $W_5O_{15}H_2$ may be represented thus :



The Action of Hydroxylamine on a Soluble Tungstate.

When hydroxylamine hydrochloride is introduced into a solution of sodium tungstate a white precipitate is obtained, which is faint yellow on drying. It does not appear to be crystalline. In water it is moderately soluble, so that the washing which is necessary in its preparation is quite wasteful. Our preparations were washed with very cold water till chlorine was removed, then with alcohol and ether, and dried in the air. The compound decomposes rather violently, but without detonation, when it is heated. The analyses agree closely with the formula



indicating simply a hydroxylamine tungstate. There appears to be no other tungstate of this type, the ammonium salt, $4(NH_4)_2O \cdot 3WO_3 \cdot 3H_2O$, mentioned by Gmelin-Kraut, really possessing another formula.¹

¹ Gmelin-Kraut: *Handbuch der Chemie*, 2., 9, 115; see *Ann. chim. phys.*, [3], 69, 23.

- I. 0.2375 gram substance gave 0.1869 gram WO_3 .
- II. 0.2621 gram substance gave 0.2046 gram WO_3 .
- III. 0.8603 gram substance gave 47.8 cc. moist N at 16°C . and 714.2 mm.
- IV. 1.3079 gram substance gave 74.5 cc. moist N at 20°C . and 717.5 mm.
0.9880 gram substance gave, on combustion, 0.1795 gram H_2O .
1.1054 grams substance lost, at 100°C ., 0.0669 gram.
- V. 1.3298 gram substance gave 1.0575 gram WO_3 .
1.0009 gram substance gave, on combustion, 0.1816 gram H_2O .
1.0343 gram substance gave 57.6 cc. moist N at 25.8°C . and 720.5 mm.

Table VI.

	I.	II.	Found. III.	IV.	V.	Calculated for $4\text{NH}_4\text{OH}$. Average. $3\text{WO}_3 \cdot 3\text{H}_2\text{O}$.	
Nitrogen			6.18	6.28	6.05	6.17	6.33
Total water ¹				(18.17)	(18.15)	(18.16)	(18.32)
Water of crystalliza- tion				6.05		6.05	6.11
H in excess of that in the crystal water				1.35	1.35	1.35	1.35
WO_3	78.70	78.05			79.52	78.75	78.96
O in excess (by diff.)						7.69	7.24

Summary.

1. WO_3 is reduced with greater difficulty than MoO_3 and CrO_3 . In alkaline solution it is not reduced by grape sugar, hydroxylamine, or metallic aluminium. Hydroxylamine simply forms a sparingly soluble tungstate. Hydrochloric acid, with either oxalic acid or alcohol, is without reducing action, and the same is true of sulphurous acid in sealed tubes.

2. Fuming hydriodic acid or stannous chloride solution re-

¹ Obtained by combustion with copper oxide.

duces tungstic acid to an insoluble indigo-blue hydroxide, $W_2O_7 \cdot H_2O$. It is readily oxidized by the air and oxidizing agents, and dissolves in hot caustic alkalis with evolution of hydrogen. It finds an analogue in the blue hydroxide of molybdenum, $Mo_3O_{11} \cdot 6H_2O$, and may be considered as the mother-substance of one of the series of tungsten bronzes having the general formula $W_3O_{11} \cdot M_2O$. It is this compound which is formed by nascent hydrogen in the well-known test for tungsten.

3. When the above compound is acted upon by strong ammonia water, a part of the tungsten dissolves out as ammonium tungstate, and there remains a brown residue which dries to a beautiful purple powder with a decided bronze luster. Its formula is $W_3O_8 \cdot H_2O$. Its chemical properties are similar to those of the blue compound. Among the oxides of uranium we find the analogous $U_3O_8 \cdot xH_2O$, and the series of tungsten bronzes of the general formula, $W_3O_{11} \cdot M_2O$, may be looked upon as its derivatives.

This work is published in an unfinished condition because the authors were obliged to separate. It is the intention of one of us to carry on further studies in this field.

MISSOURI STATE SCHOOL
OF MINES.

Contribution from the Chemical Laboratory of Wesleyan University.

A CHEMICAL METHOD FOR OBTAINING VACUA.

BY FRANCIS G. BENEDICT AND CHARLOTTE R. MANNING.

The production of a "good" vacuum, especially in desiccating apparatus, is frequently required in the chemical laboratory. Mechanical air pumps, so successfully used in the exhaustion of incandescent light bulbs, are obviously impracticable for ordinary laboratory use, and the valve pump of the physical lecture table is, in general, the most available form of pump for producing a vacuum. In the chemical laboratory one has, as a rule, to be content with the vacuum obtained by means of one of the many forms of water pumps unless, as is occasionally the case, a mercury pump is at hand. The length of time required to exhaust a vessel by means of the mercury pump is considered so great an objection to its

every day use that the apparatus is commonly allowed to become dirty and ultimately inoperative, awaiting a special and pressing need before being put in working order.

Though water pumps are almost universally adopted as the most practicable instrument for producing vacua in the laboratory, their use is attended with numerous difficulties, chief of which is the irregularity in water pressure, resulting in a too frequent "sucking back" of water, especially towards the end of an exhaustion. Where great inequalities in water pressure are common, it is customary to insert an empty bottle between the pump and the vessel to be exhausted to collect any water that may inadvertently be sucked back. This bottle, while serving its original purpose, obviously increases the volume of air to be removed, and consequently the time required to complete the operation.

With constant and high water pressure and otherwise ideal conditions, few, if any, forms of water pump will give a vacuum corresponding to a mercury pressure of less than 10 mm.

It is more frequently the case, however, that the water pump available at any particular time falls far short of this efficiency, and, indeed, by being so inferior, materially delays the drying operation that is dependent on a good vacuum.

So far as we are aware, the use of chemical means for obtaining vacua has never been generally adopted. The absorption of a gas or vapor filling a space by means of some suitable non-volatile absorbent is, however, capable of yielding vacua of the highest degree of perfection.

Regnault,¹ in some of his experiments on hygrometry, made use of the absorbing action of concentrated sulphuric acid towards aqueous vapor to produce a vacuum. He exhausted a large glass globe in which a few grams of water had been placed until all the water had vaporized, thereby expelling the air. By shaking the globe, he was able to break a small glass bulb which had previously been filled with concentrated sulphuric acid, hermetically sealed and inserted in the large globe. The concentrated acid rapidly absorbed the water vapor, thereby producing a very perfect vacuum.

¹ *Ann. chim. phys.*, [3], 18, 190 (1845).

The absorption by potassium hydroxide of residual carbon dioxide in a vessel previously filled with the gas, and then partially exhausted, was first used by Andrews.¹

Brunner² substituted calcium hydroxide for potassium hydroxide, and made use of the fact that dry calcium oxide will not absorb dry carbon dioxide in establishing the conditions under which the operation is best conducted. At the end of the preliminary exhaustion by the water pump or air pump, the calcium oxide is moistened with a small quantity of water. The carbon dioxide is absorbed, the aqueous vapor resulting being finally absorbed by concentrated sulphuric acid in a dish at the bottom of the vessel to be exhausted. In two hours a nearly perfect vacuum was thereby obtained in a half-liter vessel of special construction.

He further suggests the use of ammonia in the place of carbon dioxide, absorbing the gas by concentrated sulphuric acid.

Newth³ has adopted this suggestion in a very striking lecture experiment, though the practicability of this method as a laboratory agent is very doubtful.

Pflüger⁴ demonstrated very clearly the agency of water vapor in removing air from a vessel during the process of exhaustion. In an apparatus of special construction he vaporized water by exhausting the air by means of a water pump. On introducing concentrated sulphuric acid he was able to lower the tension of the residual gas to 1 or 2 mm. of mercury. He suggests the introduction of concentrated sulphuric acid into vacuum desiccators after, and not before, exhaustion, though no description of a practical apparatus involving the use of this principle is included in his article.

Other applications of chemical reactions in obtaining vacua with special reference to perfecting the Torricellian vacuum include those of Gassiot,⁵ who used metallic sodium in a rarefied atmosphere of pure oxygen, and applied Andrews'⁶ method

¹ Phil. Mag., 1852, p. 104; Ann. Phys. und Chem., 88, 309 (1853).

² Ann. Phys. und Chem., 94, 523 (1855).

³ "Chemical Lecture Experiments," London, 1892, p. 58.

⁴ Archiv. f. die Ges. Physiologie, 38, 311 (1886).

⁵ Phil. Trans., 149, 147 (1859).

⁶ Loc. cit.

to the preparation of vacuum tubes,¹ and Crookes,² who used sulphur to absorb mercury vapor and copper to absorb any traces of sulphur vapor.

While not, strictly speaking, the result of chemical agency, the absorption of the residual gas by charcoal, as suggested by Dewar and Tait,³ the freezing of the mercury vapor in a Torricellian vacuum by liquid air,⁴ and the freezing of air by liquid hydrogen,⁵ as shown by Dewar, should be mentioned.

In determining the amount of water in organic compounds, especially those of a physiological nature, the greatest precaution is necessary to prevent overheating and consequent partial disintegration of the complex molecule, and, on the other hand, it is a well-known fact that many bodies of an organic nature persistently retain moisture, necessitating prolonged drying *in vacuo*. In such instances, the more perfect the vacuum the more rapid and complete the drying.

When the effect of a vacuum is accompanied by the use of a powerful dehydrating material, to absorb the water vapor constantly arising from the material undergoing desiccation, the conditions for rapid and complete drying are ideal.

Cooke and Richards⁶ pointed out the necessity of placing the drying agent in the upper portion of the space to be dried.

Hempel⁷ gave a striking experiment to show quantitatively the advisability of this disposition of the drying agent, and devised his admirable and well-known vacuum desiccator,⁸ which is constructed on this principle. In all our work this form of desiccator has been used.

A small mercury manometer was placed inside the desiccator to indicate the degree of exhaustion. With the water pump at our disposal, the air could only be rarefied to a pressure of about 40 mm. The large size of the apparatus precluded the use of a mercury pump for rapid work, and a

¹ Proc. Roy. Soc., 10, 244 (1866).

² Phil. Trans., 189, 300 (1878).

³ Proc. Roy. Soc., Edinburgh, 8, 348 (1875).

⁴ Proc. Roy. Inst., 14, 1.

⁵ Proc. Roy. Soc., 64, 231 (1898).

⁶ Proc. Am. Acad., 23, 159 (1887).

⁷ Ber. d. chem. Ges., 23, 3566 (1890).

⁸ Ztschr. angew. Chem., 1891, p. 201.

chemical means for securing the desired diminution in pressure was ultimately used.

We have found that, after expelling the air in the desiccator with ether vapor, the residual vapor is entirely absorbed by the sulphuric acid in the upper chamber, yielding a remarkably good vacuum.

The exact conditions under which the operation is best conducted are as follows:

Fresh, concentrated sulphuric acid (about 150 cc.) is placed in the previously cleaned and dried upper compartment of the desiccator. After introducing the material to be dried (in appropriate containers), and just before the cover is put in place, 10 cc. of pure anhydrous ether are delivered from a pipette upon the bottom of the desiccator in such a manner as not to come in contact with the material to be dried. The cover is then carefully put on, the glass stop-cock being left open. Immediately the water pump is connected with the tube in the cover and the exhaustion continued until the manometer shows from 40 to 60 mm. pressure. The stop-cock is then closed, the tube connecting with the water pump removed, and the desiccator allowed to stand. In a very few minutes a vacuum of from 4 to 1 (or even less) mm. is obtained. With the desiccators in use in this laboratory, this degree of exhaustion is obtained in from eight to twelve minutes after putting the cover on the desiccator.

After the water pump has been disconnected, the absorption of the ether vapor may be considerably accelerated by so rotating the desiccator held in the hands as to agitate the acid and moisten a larger surface of glass in the top compartment. Obviously this procedure can only be carried out with due care for the stability of the dishes in the desiccator.

In the size of apparatus used in our experiments the lower compartment, representing the efficient space for desiccating, contains 2100 cc.; this, together with the 1400 cc. of space in the upper compartment when containing 150 cc. of acid, gives a total gas volume of 3.5 liters to be exhausted.

Obviously a desiccator of the Hempel type is especially advantageous for use in connection with this method for obtain-

ing vacua, as the ether vapor completely fills the lower compartment, expelling the lighter air before the sulphuric acid in the upper compartment effects any great absorption of the ether vapor. Indeed it is doubtful if the method can be used with anything like this degree of efficiency with desiccators of any other type. We have found these desiccators to be remarkably tight, vacua of about 1 mm. pressure being unchanged at the end of two weeks.

We have no data as to how many charges of ether 150 cc. of sulphuric acid will absorb, but the same acid has been used in the operation of exhausting the desiccator three times with no noticeable diminution in the efficiency of absorption.

This method is especially adapted for use in the chemical laboratory, for (1) the apparatus required is that already in use in many laboratories, (2) the time requirement to secure a good vacuum is reduced to a minimum, and (3) no ordinary method will permit of so complete a rarefaction of the gases in the desiccator.

The application of this method in obtaining high vacua other than in desiccators has more to do with the physicist than the chemist, the only object of this paper being to present to the chemical laboratory a simple and rapid means for obtaining a good vacuum.

MIDDLETOWN, CONN.

Contributions from the Sheffield Laboratory of Yale University.

XCVI.—ON THE MIXED CRYSTALS OF SILVER CHLORATE AND SODIUM CHLORATE, AND THEIR SOLUTIONS.

BY H. W. FOOTE.

I.

In a previous article¹ it has been shown that when two salts crystallize from aqueous solution, depositing mixed crystals of two crystalline forms, the composition of the crystals at the mixing limit should, in general, change with the change of temperature. Experiments to prove this were carried out

¹ This JOURNAL, 26, 418 (1901).

with mixed crystals of copper and zinc sulphates. In the present investigation one of the objects has been to show that the composition of mixed crystals of silver chlorate and sodium chlorate at the mixing limit changes with change of temperature.

Retgers has shown¹ that silver chlorate and sodium chlorate form mixed crystals very readily. He found that sodium chlorate crystallizes in cubes containing up to 11 molecular per cent of silver chlorate, while silver chlorate crystallizes in the tetragonal system, containing as much as 41.75 molecular per cent of sodium chlorate. The temperature of the experiments was the ordinary room temperature. As will be shown later, these values are slightly below the real mixing limits for that temperature.

In the experiments to be described, pure sodium chlorate and silver chlorate were required. The former was prepared by recrystallizing the commercial product, which contained a small amount of chloride. Barium chlorate was the starting point for silver chlorate. To a solution containing a known amount of the barium salt, a calculated quantity of sulphuric acid was added, just sufficient to precipitate all the barium as sulphate. The precipitate was removed by filtration, and the filtrate, containing practically pure chloric acid in solution, was saturated with silver carbonate, prepared by precipitating silver nitrate with sodium carbonate. The solution of silver chlorate was filtered from the excess of silver carbonate, evaporated, and silver chlorate obtained by crystallization. The product was purified by repeated crystallization. It was found, on analysis, to be pure.

In determining the mixing limits of the two forms, solutions were used having a volume of 300 to 400 cc. A small quantity of crystals forming from this volume of solution would alter the composition of the mother-liquor but very slightly. The relative proportions of the two salts in solution were varied until both cubes and tetragonal crystals formed at the same time in approximately equal amount. The two forms of crystals were so unlike that they could be distinguished at a

¹ *Ztschr. phys. Chem.*, **5**, 438 (1890).

glance and separated mechanically. It was usually found best to add a minute quantity of the two salts to start the crystallization, and those crops only were analyzed in which both forms could be obtained pure.

Silver chlorate was determined in the crystals by titration with ammonium thiocyanate, and sodium chlorate by difference. The solutions were analyzed by evaporating weighed quantities to dryness and heating in an air-bath at about 120°. The residue, after weighing, was dissolved in water and titrated with thiocyanate solution, to obtain the amount of silver chlorate present. Sodium chlorate was then calculated by difference.

The experiments were carried out at 12°, 25°, 35°, and 50°. An Ostwald thermostat was used for the three higher temperatures, while for 12° a thermostat which I have previously described¹ was used. The latter ran constantly for a month or more with practically no attention and maintained a very even temperature.

In tabulating the results (Table I.) the mixing limits of the two forms of crystals are given in the first and second columns. The number of molecules of sodium chlorate and of silver chlorate to 100 molecules of water are given in the third and fourth columns, respectively, representing the composition of the solutions from which the two forms of crystals were obtained, while in the fifth column is given the molecular percentage of sodium chlorate in the total amount of dissolved silver and sodium chlorates in the solutions. The four analyses for each temperature were made from separate crops of crystals. The following results were obtained:

Table I.—*Mixing Limits of Cubes and Tetragonal Crystals of Sodium and Silver Chlorates.*

Tetragonal. Molecular per cent of NaClO ₃ .	Cubes. Molecular per cent of NaClO ₃ .	Mols. NaClO ₃ : 100 mols. H ₂ O.	Mols. AgClO ₃ : 100 mols H ₂ O.	Molecular per cent NaClO ₃ in dissolved chlorates.
T = 12°.				
49.13	85.54	13.85	0.249	98.23
50.45	84.41	13.87	0.301	97.87
50.85	85.48	14.01	0.289	97.98
49.71	87.26	14.14	0.291	97.98

¹ Ztschr. phys. Chem., 33, 749 (1900).

Tetragonal. Molecular per cent of NaClO_2	Cubes. Molecular per cent of NaClO_2	Mols. NaClO_2 : 100 mols. H_2O .	Mols. AgClO_2 : 100 mols. H_2O .	Molecular per cent NaClO_2 in dissolved chlorates.
$T = 25^\circ$.				
48.27	81.12	15.35	0.418	97.35
48.61	81.63			
48.08	83.52			
47.80	79.94	15.59	0.481	97.01
$T = 35^\circ$.				
48.65	81.02	17.28	0.568	96.81
47.45	79.03	17.26	0.737	95.91
47.84	76.61	16.66	0.596	96.55
47.73	76.43	16.87	0.645	96.32
$T = 50^\circ$.				
47.27	74.08	19.34	1.019	95.00
47.78	75.96	19.42	0.966	95.26
47.13	74.77	19.35	0.980	95.18
46.20	68.93			

The results, especially those for the cubes, vary considerably among themselves, as a very slight change in the composition of the solutions produces a very large change in the mixed crystals. The average values for each temperature are given in Table II., and it is believed that these represent very nearly the true mixing limits.

Table II.—Averages Computed from Table I.

Temp.	Tetragonal. Molecular per cent of NaClO_2	Cubes. Molecular per cent of NaClO_2	Mols. NaClO_2 : 100 mols. H_2O .	Mols. AgClO_2 : 100 mols. H_2O .	Molecular per cent NaClO_2 in dissolved chlorates.
12°	50.04	85.67	13.97	0.283	98.02
25°	48.19	81.55	15.47	0.450	97.18
35°	47.92	78.27	17.02	0.636	96.40
50°	47.10	73.44	19.37	0.988	95.15

The results in Table II. are shown graphically in Fig. I., where the temperatures are plotted as ordinates and the molecular percentages of sodium chlorate at the mixing limit as abscissas. It is quite evident that the mixing limit varies with the temperature, though in the case of the tetragonal crystals the change is very slight. The curve *AB*, representing the varying composition of the cubes at the mixing limit, is a straight line. If continued downward, it would inter-

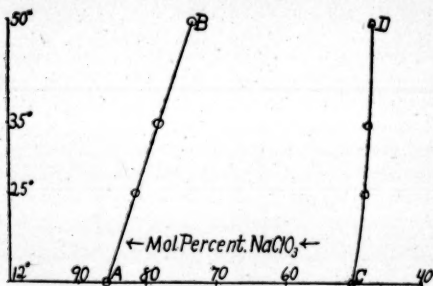


Fig. I.

sect the temperature axis at about -30° , that is, at -30° sodium chlorate in cubes should be unable to form mixed crystals with silver chlorate. This would make it appear very probable that the crystalline form of sodium chlorate changes at this temperature. The curve CD shows that as the temperature is lowered tetragonal silver chlorate can take up increasing amounts of sodium chlorate. It thus seems most probable that sodium chlorate would assume the tetragonal form below -30° , and be completely isomorphous with silver chlorate. If this interpretation of the results be correct, it indicates a method of determining the transition temperature of a salt by means of its mixed crystals.

II.

A second object of this investigation has been to determine the relations existing between the salts in solution and the mixed crystals. In what follows, I shall use the following symbols: y represents the molecular percentage of the more soluble salt, as sodium chlorate, in the total amount of dissolved salts, and x the molecular percentage of that salt in the mixed crystals. Roozeboom has shown¹ that when mixed crystals form in two different crystalline modifications, as is the case with sodium and silver chlorates, the solutions from which the two forms are deposited are of two classes as regards the mixed crystals:

¹ Ztschr. phys. Chem., 8, 504 (1891).

I. The value of y , when the solution deposits both forms of crystals, lies between the values of x for the two forms at the mixing limit (Case IV. of Roozeboom).

II. The value of y is greater than either of the values of x at the mixing limit (Case V. of Roozeboom).

Roozeboom investigated¹ solutions of potassium and thallium chlorates, and the mixed crystals formed from them, and found they belonged to Class I., as is evident from the following values:

$$y = 93.25,$$

$$x = 36.30 \text{ and } 97.93.$$

In this case y represents the percentage of potassium chlorate in the dissolved chlorates, and x the percentage of potassium chlorate in the two crystallized forms at the mixing limits. It will be noticed that y lies between the two values of x . Similar results have been obtained by Muthmann and Kuntze² with the permanganates of potassium and rubidium, and by Fock³ with the following pairs of salts: Potassium and ammonium chlorides, potassium and ammonium bromides, potassium and thallium nitrates, and copper and nickel sulphates. In this class, solutions depositing crystals of one form only, when concentrated, change their proportions of salts till they reach a concentration where both forms of mixed crystals are deposited together. On further evaporation the composition of the solution remains fixed and both forms crystallize together as long as any solution remains. It will be noticed, by reference to Table II., that the value of y , representing the molecular percentage of sodium chlorate in the solutions, is greater than either value of x , the molecular percentage of sodium chlorate in the mixed crystals. Evidently this example belongs under Class II., though Roozeboom⁴ was inclined to believe, from the work of Retgers, that the salts belonged in the first class, behaving like thallium and potassium chlorates. I believe only one example of this class has previously been described, that of the mixed double chlorides of copper with ammonium and potassium by

¹ *Ztschr. phys. Chem.*, 8, 531 (1891).

² *Ztschr. f. Kryst.*, 23, 368.

³ *Ibid.*, 28, 337.

⁴ *Ztschr. phys. Chem.*, 8, 528 (1891).

Fock.¹ In this class, when a solution is concentrated, the proportion of the more soluble salt will increase in the solution as water is removed, till the solution is completely evaporated.

It seemed desirable to show (1) whether the relation $y > x$ holds true for the chlorates at all points where the concentration of the solution is such that only one form of crystal is deposited, and (2) what is the influence of temperature on the relative values of y and x . Solutions containing different proportions of silver and sodium chlorates were accordingly prepared in such concentrations that a small amount of mixed crystals separated at the temperature desired. The volume of the solutions was, as before, 300 to 400 cc. The experiments were carried out in the thermostat as before.

The following results were obtained (Table III). The values at the mixing limits are taken from Table II.

Table III.

Tetragonal. Molecular per cent of NaClO ₃ .	Cubes. Molecular per cent of NaClO ₃ .	Mols. NaClO ₃ : 100 mols. H ₂ O.	Mols. AgClO ₃ : 100 mols. H ₂ O.	Molecular per cent of NaClO ₃ in dissolved chlorates. y .
x_1 .	x_2 .			
$T = 12^\circ$.				
....	94.45	14.73	0.111	99.23
....	92.76	14.39	0.165	98.87
....	90.15	14.30	0.197	98.64
50.04	85.67	13.97	0.283	98.02
42.05		9.22	0.360	96.24
32.12		6.89	0.478	93.52
13.11		3.61	0.550	86.77
5.04		1.46	0.695	67.79
$T = 25^\circ$.				
....	93.65	16.93	0.232	98.65
....	85.06	16.14	0.385	97.67
48.19	81.55	15.47	0.450	97.18
31.97		8.37	0.742	91.85
25.74		7.34	0.798	90.19
9.71		3.62	1.03	77.77
4.00		2.37	1.14	67.46
3.04		1.72	1.17	59.55

¹ Ztschr. phys. Chem., 12, 657 (1893).

Tetragonal. Molecular per cent of NaClO_3	Cubes. Molecular per cent of NaClO_3	Mols. NaClO_3 : 100 mols. H_2O .	Mols. AgClO_3 : 100 mols. H_2O .	Molecular per cent of NaClO_3 in dissolved chlorates.
x_1	x_2			y

$T = 35^\circ$.

....	98.00	19.14	0.090	99.53
....	95.20	18.60	0.196	98.94
....	91.72	18.12	0.310	98.29
....	89.77	17.91	0.338	98.15
....	88.24	17.83	0.431	97.64
47.92	78.27	17.02	0.636	96.40
46.81		16.02	0.637	96.17
42.11		12.82	0.804	94.10
37.20		11.20	0.941	92.25
23.09		7.59	1.16	86.76
12.06		4.69	1.38	77.25
5.86		3.31	1.49	68.98
3.66		2.33	1.65	58.49

$T = 50^\circ$.

....	94.27	21.15	0.289	98.65
....	79.86	19.59	0.875	95.73
47.10	73.44	19.37	0.988	95.15
42.69		16.02	1.25	92.76
34.87		12.67	1.54	89.18
17.71		7.80	2.08	78.97
6.60		4.06	2.37	63.09
3.38		1.98	2.85	41.04

It will be noticed that for all temperatures the values of y are greater than the corresponding values of x , that is, the proportion of sodium chlorate in the solutions is always greater than in the mixed crystals which are deposited from them.

In Fig. II., the values of x and y taken from Table III. are plotted as abscissas and ordinates, respectively, for the temperatures 25° and 50° . From the diagram it is evident that as the temperature rises the values of x and y become more nearly equal, that is, the composition of the mixed crystals will approximate more nearly to the composition of the solutions from which they form.

The following conclusions may be drawn from the results as regards obtaining the pure salts from the mixed crystals by recrystallization: Silver chlorate could be obtained prac-

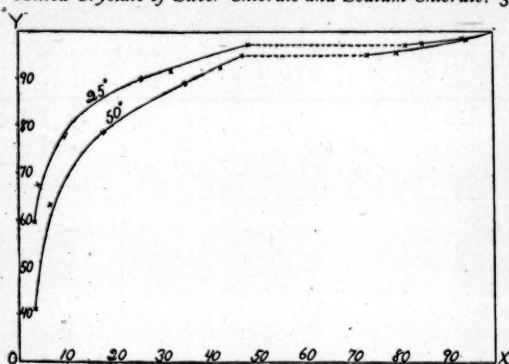


Fig. II.

tically pure by recrystallizing, as the proportion of it in the crystals is always greater than in the solution. On the other hand, to obtain pure sodium chlorate by recrystallizing the mixed crystals would be impossible, even though the mixed crystals at first were nearly pure sodium chlorate. The recrystallized product would always contain more silver chlorate than the mother-liquor. In this case a purer product would be obtained by evaporating the mother-liquor than from the recrystallized product. Silver chlorate could be obtained more readily in a pure condition if the recrystallization were carried on at a low temperature, for the proportion of silver chlorate in the mixed crystals deposited from a given solution is greater, the lower the temperature.

Summary.

1. The composition of mixed crystals of sodium and silver chlorates at the mixing limit changes with a change in temperature.
2. The percentage of sodium chlorate in the total amount of dissolved chlorates in a solution is greater than in the mixed crystals from the solution.
3. As the temperature is raised the percentage of sodium chlorate in the total amount of dissolved chlorates becomes

more nearly equal to the percentage of this chlorate in the mixed crystals.

4. Silver chlorate may be obtained pure by recrystallizing the mixed chlorates.

5. Sodium chlorate cannot be obtained pure by recrystallizing the mixed chlorates, for the recrystallized product contains more silver chlorate than the mother-liquor.

THE ELECTROMOTIVE FORCE OF METALS IN SOLUTIONS OF CYANIDE.¹

By S. B. CHRISTY.

In reviewing my paper "On the Solution and Precipitation of Cyanide of Gold,"² Mr. E. B. Wilson contends³ that "in the solution of gold by means of alkaline cyanides the various reactions are determined as to their order and intensity by the relative positions of the elements concerned in the electrochemical series, or series of voltaic tension."

In a modified form this statement is probably true. That is to say, the difference of electrical potential in any closed electrical circuit determines the nature of the reactions which ensue. But the matter is not so simple as Mr. Wilson assumes. Recent investigations show that the order of the metals in the electrochemical series depends not only on the nature of the elements themselves, but also on the chemical composition of the solution in which they are placed, its degree of concentration, its temperature, and, in the case of gases, on the pressure.

Unless all these conditions are taken into account, inferences drawn from the electrochemical series are likely to prove more misleading than useful. The series, as quoted by Mr. Wilson from Gore, is as follows:

3 Potassium	28 Antimony
4 Sodium	29 Tellurium
8 Calcium	31 Gold
9 Magnesium	37 Carbon

¹ Communicated by the author and based upon an article in the Transactions of the American Institute of Mining Engineers, Vol. 30.

² Trans. Am. Inst. Min. Eng., 26, 735.

³ *Ibid.*, 27, 821.

12 Manganese	39 Nitrogen
13 Zinc	40 Arsenic
15 Iron	43 Sulphur
20 Lead	45 Bromine
24 Copper	46 Chlorine
25 Hydrogen	47 Oxygen
27 Silver	

This series correctly shows the difference of potential in many solvents, especially in acid solutions, but the use of it for predicting the action of cyanide solutions involves several grave errors, one of which is the assumption that the nature of the solution in which substances are placed is without effect on the order of the series.

The remarkable effect of solutions of cyanide of potassium upon the relative positions of substances in the electrochemical series was first shown by Prof. Jacoby, who, on August 21, 1844, called the attention of the St. Petersburg Academy of Sciences to the fact that when silver and cyanide of potassium solution replace the zinc and sulphuric acid in the Daniell cell, a strong current ensues and copper is precipitated. Ordinarily, and according to the usual inference from the above series, copper precipitates silver from its solutions, but here was a combination in which silver precipitated copper.

In the following year, Poggendorff announced¹ that by his (now well-known) "compensation method," he had found the electrochemical series in 1 part of potassium cyanide to 8 parts water—*i. e.*, in a 12.5 per cent solution of potassium cyanide, to be :

1 Zinc amalgamated	9 Lead
2 Zinc	10 Mercury
3 Copper	11 Palladium
4 Cadmium	12 Bismuth
5 Tin	13 Iron
6 Silver	14 Platinum
7 Nickel	15 Cast-iron
8 Antimony	16 Carbon

Gore² also investigated this subject with similar results, only

¹ Pogg. Ann., 66, 597 (1845).

² Proc. Roy. Soc. (London), 30, 45 (1879).

he showed that the order depends on concentration and temperature, and that, according to these conditions, gold may be more or less electro-positive than silver.

The variations thus discovered in the relative position of the metals in the electrochemical series at once cast a cloud on its usefulness for predicting chemical reactions; and though a great mass of experimental data was accumulated, and the most acute minds of the century were brought to bear on the problem, no explanation of these anomalies was found for many years.

It is only within the last decade that anything like a clue to the mystery has been detected; and this result has been made possible only through the combined efforts of a number of men who approached the subject from what may be almost termed its purely speculative side, without any thought of practical applications.

Methods Used in This Investigation.

In looking about for some means of determining the relative affinities of the metals for cyanide solutions, I long ago came to the conclusion that the determination of the relative electromotive forces of the metals in solutions of different strengths was the simplest, readiest, and most certain that could be selected. For, properly considered, it shows the actual tendency of the metal to go into solution. My first experiments were made in this direction in August, 1896. I made at that time a large number of preliminary determinations, the results of which were presented in a lecture given February 1, 1897, before the California Academy of Sciences, in San Francisco.

The results of these experiments have filled me with constant surprise, when I have noticed what apparently slight causes were capable of making great changes in the electromotive force of the same metal. The great delicacy of the method proved to be the chief source of difficulty in its application, while at the same time it reported faithfully the facts as they exist in nature.

Two methods have been used in these determinations, the first being what I have, for brevity, called the "Deflection"

method, and the other the "Compensation" or "Zero" method of Poggendorf.

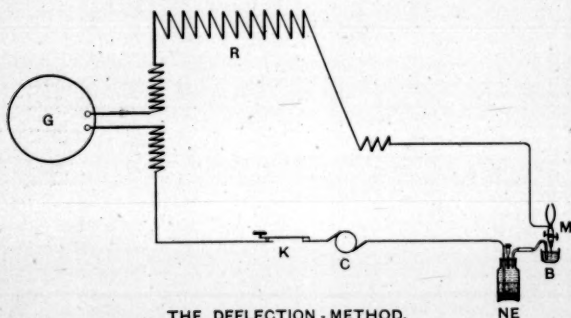
In each case an electrolytic cell is constructed with two electrodes, each immersed in a separate solution. One, consisting of the metal to be tested, was held in the points of a platinum-tipped pair of forceps, electrically connected with a galvanometer, and was immersed in a vessel containing the cyanide solution of the given strength. The other was in all cases the "normal" electrode of Prof. Ostwald, consisting of mercury, electrically connected with the galvanometer by means of a glass-coated platinum wire. The surface of the mercury is covered with a layer of mercurous chloride, a couple of inches thick, and a solution of chloride of potassium of 1 gram-molecule $\frac{M}{I}$ (in this case also a normal solution).

The purpose of the normal electrode of Ostwald is to have a non-polarizable electrode in a solution of known strength and electromotive force. This is fixed at -0.560 volt. That is, in the case of the normal electrode, the mercury ions tend to precipitate themselves on the surface of the mercury, and the solution is therefore negative to the metal by 0.560 volt. That is, the positive current tends to flow through the solution to the mercury, which becomes positively electrified, while the solution itself becomes negatively electrified.

If we neglect the slight electromotive force due to the contact of the two solutions, the resulting electromotive force of the combined cell is the algebraic sum of the electromotive forces active at the two electrodes. Hence, if we subtract 0.560 from the electromotive force of the cell, we have the electromotive force of the metal under consideration. The algebraic sign indicates the direction of the positive current.

The Deflection Method.—This method is much the most convenient for such investigations, particularly in the first roughing out of a large amount of material. With proper precautions it gives results not less reliable than those obtained by the zero method, and it has the great advantage over the latter that the rapid changes of electromotive force may be followed almost as they occur.

The method is illustrated in Fig. I. B is the cell containing the cyanide solution and the metal M to be tested, NE is Ostwald's normal electrode, R is a resistance which varied in the tests from 30,000 to 200,000 ohms, G is a Wiedemann reflecting galvanometer, K, a make-and-break circuit key, and C a commutator.



- | | |
|--------------------------------------|---|
| B, Cell Containing Cyanide Solution; | R, Resistance of from 30,000 to 200,000 Ohms; |
| M, Metal to be Tested; | G, Wiedemann's Reflecting Galvanometer; |
| NE, Ostwald's Normal Electrode; | K, Make - and Break - Circuit Key. |

Fig. I.

The galvanometer was calibrated by replacing the cells B and NE with a Clark cell, prepared according to the directions of Ostwald, and noting the deflection produced by its voltage through the given resistance of 30,000 to 200,000 ohms. The voltage was taken as electromotive force = 1.438—0.001 (t° —15° C.) volts.

Most of the concentrations of potassium cyanide were $\frac{M}{1}$ (one gram-molecule, 65 grams per liter, or 6.5 per cent), or fractional multiples of this in tenths. Thus the series used was frequently $\frac{M}{1}$, $\frac{M}{10}$, $\frac{M}{100}$, $\frac{M}{1,000}$, $\frac{M}{10,000}$, $\frac{M}{100,000}$, $\frac{M}{1,000,000}$.

As there is no little difference in the methods of notation in use, and much resulting confusion, the following methods of notation will always be used in this paper: We shall follow the motion of the positive ions through the solution, and the mode of notation will depend entirely on that. When the motion of the positive ion in the solution is from the metal to the solution, the metal is said to be electropositive, because it gives up positive ions to the solution and causes the solution to become positively electrified, itself becoming at the same time negatively electrified. Such, for instance, is the case of zinc in a solution of zinc sulphate. When, on the other hand, the solution gives up positive ions to the metal immersed in it, as is the case with copper in a solution of copper sulphate, the metal is said to be electronegative, for it causes the solution in which it is immersed to become electronegative, itself, at the same time, becoming positively electrified. The mercury in Ostwald's normal electrode is another example. The + or - sign, then, here indicates the direction of ionic motion, and simply shows whether the given positive ions tend to flow away from the metal into the solution or towards the metal from the solution. That is, whether the "solution pressure" of the metal is greater or less than the "osmotic pressure" of the ions in solution.¹

Now, when an electropositive and an electronegative metal are coupled, the direction of flow of the ions of both through the solution is the same, and the electromotive force of the combination is the arithmetic sum of those of the ingredients. When two electropositive or two electronegative metals are coupled, the ions tend to flow through the solution in opposite directions; hence, the electromotive force of the combination is equal to the arithmetic difference between the separate electromotive forces, the direction of motion, and hence the sign, being that of the greater.

In combinations in which the Ostwald normal electrode is one member, we know the amount and direction of one electromotive force, and hence, when we measure that of the combination, it is easy to calculate that of the other (neglecting

¹ With regard to the anions, the + and - signs have an inverse meaning.

the slight electromotive force due to the contact of the solutions).¹

Thus, if, against the normal electrode, aluminum in a $\frac{M}{I}$ solution of potassium cyanide gives an electromotive force = +1.55 volts,—that is, if the current flows from the aluminum to the mercury, the same as in the case of mercury,—it follows that the electromotive force of the aluminum in $\frac{M}{I}$ potassium cyanide will be +1.55 — 0.560 = +0.99 volts.

Again, if a strip of amalgamated zinc under similar circumstances gives a voltage of +1.49 volts, the electromotive force of amalgamated zinc in a $\frac{M}{I}$ potassium cyanide solution will be +1.49 — 0.560 = +0.93 volt.

In making the determinations, it must be evident from the formula that, if there are few ions of the given metal present in the solution at the start, the introduction of a very few more will make great changes in the value of the electromotive force.

For in $\log \frac{P}{p}$ it must be evident that as P the solution tension is constant (for a given temperature), the value will depend entirely upon p , the osmotic pressure, and the smaller p is, the greater will be the effect due to slight changes in p . Hence, it will be impossible to get constant values for the electromotive force, unless the value of p is nearly constant; that is, when the solution is saturated with ions at the given temperature. That is the case with the normal electrode, where the mercury lies in a saturated solution of mercurous chloride. The mercury is thus in equilibrium with its ions, and a constant electromotive force results.

To get perfectly constant results with cyanide solutions, it would be necessary to have the solution saturated with the cyanide of the metal in question. But while this would give us a very satisfactory electromotive series, it would not give us a measure of the action of the unsaturated cyanide solu-

¹ This, except in cases of great differences in the concentration of the solutions, has been shown to cause an error of only a few thousandths or hundredths of a volt.

tion, just as it acts on the ores. We must, therefore, be content with results that are not entirely concordant, and take the best of a large number of determinations.

The strips used were always freshly burnished with sand-paper, cooled, and touched to a grounded platinum wire to discharge any electricity with which they might have been charged in burnishing.

Preliminary Results with the Deflection Method.—The following preliminary results were obtained in October to December, 1896, with some of the common metals and minerals. The metals were good commercial articles, such as are in use in the arts, except in the case of gold, silver, and mercury, which were chemically pure. In the case of some of the minerals, such as zincblende, stibnite, etc., the electrical resistance was probably so high in comparison with that of the intercalated resistance that the results may be somewhat low.

Nevertheless, they give at once some important relations which must exist whenever the cyanide process is applied in the treatment of ores:

Table I.—*Electromotive Force of Metals in Cyanide Solutions. Deflection Method. Preliminary Experiments.*

	Ostwald's normal electrode = -0.560 volt.			
	$\frac{M}{1}$ KCN. Volt.	$\frac{M}{10}$ KCN. Volt.	$\frac{M}{100}$ KCN. Volt.	$\frac{M}{1000}$ KCN. Volt.
*Aluminium	+0.99	+0.90	+0.76	+0.40
*Zinc, amalgamated	+0.93	+0.82	+0.70	+0.44
*Zinc, commercial	Not determ.	+0.77	+0.59	+0.39
*Copper	+0.81	+0.62	+0.37	+0.16
*Cadmium	+0.61	+0.57	+0.35	
Cadmium, amalgama'd	+0.55	+0.31	+0.19	
*Tin	+0.45	+0.24	+0.17	+0.06
*Bornite	+0.45	+0.25	-0.16	
Copper, amalgamated	+0.39(?)	+0.41	-0.14(?)	-0.12(?)
*Gold	+0.37	+0.23	+0.09	-0.38
*Silver	+0.33	+0.15	-0.05	-0.36
*Copper-Glance	+0.29(?)	+0.25	+0.05	-0.44
*Lead	+0.13	+0.05	+0.01	
Tin, amalgamated	Not determ.	+0.01	-0.07	-0.12
Lead, "	"		-0.03	
*Mercury	-0.09	+0.01	-0.11	
Gold, amalgamated			-0.13	-0.26

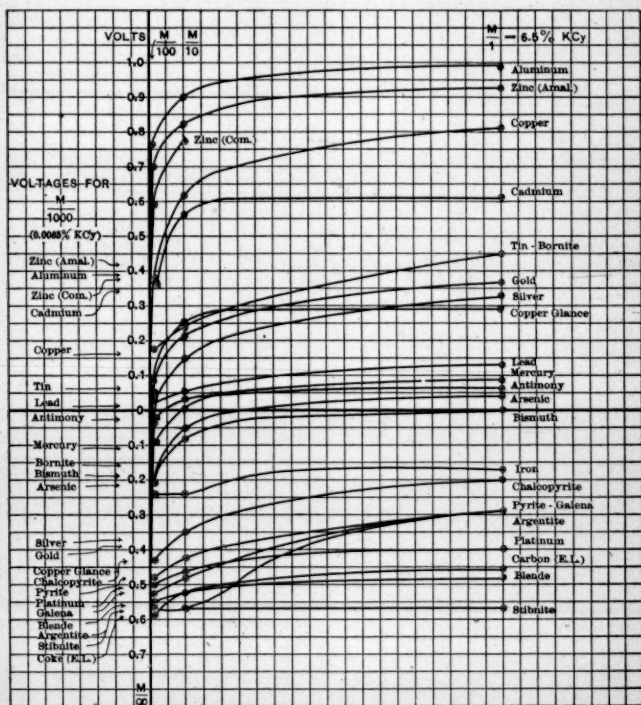
Ostwald's normal electrode = -0.560 volt.

	$\frac{M}{1} \text{ KCN.}$ Volt.	$\frac{M}{10} \text{ KCN.}$ Volt.	$\frac{M}{100} \text{ KCN.}$ Volt.	$\frac{M}{1000} \text{ KCN.}$ Volt.
*Antimony	+0.06	+0.03	-0.03	
*Arsenic	+0.04	-0.05	-0.21	
*Bismuth	+0.00	-0.06	-0.20	
Niccolite	-0.11	-0.17	-0.44	
*Iron	-0.17	-0.24	-0.24	
*Chalcopyrite	-0.20	-0.34	-0.44	
*Pyrite	-0.28	-0.42	-0.48	
*Galena	-0.28	-0.48	-0.52	
*Argentite	-0.28	-0.56	-0.55(?)	
Berthierite	-0.30	-0.52	-0.52	
Speiscobalt	-0.30	-0.33	-0.50	
Magnetopyrite	-0.30	-0.40	-0.54	
Fahlre	-0.36	-0.52	-0.52	
Arsenopyrite	-0.40	-0.45	-0.54	
*Platinum	-0.40	-0.46	-0.50	
Cuprite	-0.43	-0.55	-0.57	
*Electric light carbon	-0.46	-0.52(?)	-0.57	
*Blende	-0.48	-0.52	-0.55	
Boulangerite	-0.50	-0.55	-0.55	
Bournonite	-0.50	-0.55	-0.56	
Coke	-0.52	-0.52	-0.42(?)	
Ruby silver ore	-0.54	-0.53(?)	-0.54	
Stephanite	-0.54	-0.55	-0.52(?)	
*Stibnite	-0.56	-0.56	-0.56	

The electromotive forces of the metals and minerals marked with an asterisk in the above table have been plotted in Fig. II. The Y axis shows the potential in volts, the X axis the concentration in gram-molecules and also in percentages of potassium cyanide.

It will be noticed that in most cases the curves approximate quite closely to the logarithmic curve which theory would give, supposing the osmotic pressure of the metallic ions present to be inversely proportional to the concentration of the free potassium cyanide present, but they have different origins.

It will be noticed that the electromotive force of commercial sheet-zinc is increased by amalgamation, probably by reducing local action with some of its impurities, by which some of the current produced is short-circuited. In all the other



PRELIMINARY RESULTS. OCT. - DEC. 1896.

Fig. II.

experiments amalgamation reduces the electromotive force of the combination.

With some substances, particularly aluminium, copper, iron, platinum, and gas carbon, it was very difficult to get concordant results; with aluminum and copper this seemed to be due to a tendency to form an insoluble film on the surface of the

metal, which put a stop to further action. With copper and iron it was also possibly due to a tendency of the metals to a change of valency, which is accompanied by a change in the electrical state. With platinum and gas carbon it was not improbably due to a varying content of absorbed gas.

In testing the minerals, it was in all cases difficult to get a complete electrical contact between the tips of the platinum forceps and the rough surface of the mineral fragment, so that the results are only provisional, particularly as the resistance in some of these cases was very high. Nevertheless, the results are very interesting. They show, for instance, that not all copper minerals have a strong action on the current. Pure chalcopyrite, for instance, has hardly more action than pure pyrite, while bornite and copper glance have a very decided tendency to go into solution. Cuprite is also apparently very little acted on, though this may be due to its high resistance rather than to a lack of tendency to dissolve. The soluble salts and minerals of copper could not be tested in this manner, owing to their non-conductivity.

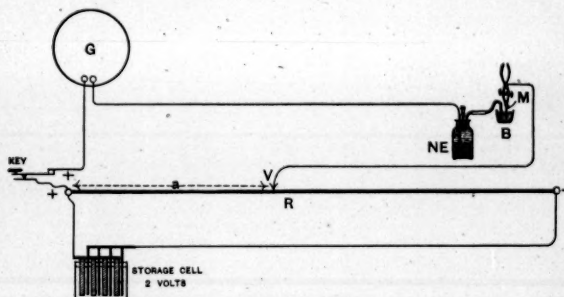
It is plain, however, that pure chalcopyrite, galena, argentite, magnetopyrite, fahlore, arsenopyrite, blende, boulangierite, bournonite, ruby silver ore, stephanite, and stibnite, when free from their oxidation-products, are apparently very little acted on by cyanide solutions.

It is also plain that a particle of metallic gold, in contact with a particle of pyrite, forms a galvanic couple in $\frac{M}{I}$ or 6.5 per cent potassium cyanide solution, equal to $+0.65$ volt, in $\frac{M}{10}$ or 0.65 per cent potassium cyanide solution, $+0.65$ volt, and in $\frac{M}{100}$ or 0.065 per cent potassium cyanide solution, $+0.57$ volt. With zinc, under the same circumstances (if we take for $\frac{M}{I}$ potassium cyanide solution the figures for amalgamated zinc), taking the zinc as the more electropositive metal, and subtracting the potential of gold, we have differences of $+0.56$ volt, $+0.54$ volt, and $+0.50$ volt. In short, these figures would measure the tendency of the zinc to

dissolve, or of the gold to precipitate in potassium cyanide solutions of these strengths.

According to these figures, the precipitating power of the zinc seems to hold up quite well for the dilute solutions. The actual failure to precipitate the gold, sometimes met with in dilute solutions, is no doubt due to films of cyanide or hydrate of zinc, which form incrustations on the surface of the zinc and thus prevent contact. The fact that the use of a small amount of fresh cyanide or of caustic potash in the zinc-boxes starts precipitation again, seems to favor this explanation.

The Zero Method.—This method is shown in outline in Fig. III. NE is the Ostwald normal electrode. B is the cell con-



POGGENDORF'S COMPENSATION - METHOD.

B, Cell Containing Cyanide Solution; R, Resistance Graduated into 10,000 Parts;
M, Metal to be Tested; V, Movable Contact;
NE, Ostwald's Normal Electrode; G, Wiedemann's Reflecting Galvanometer.

Fig. III.

taining the cyanide solution in which, as before, is immersed the metal M to be tested. At G is a galvanometer. At R is a resistance, graduated, in my experiments, into 10,000 parts. A storage battery of 2 volts and the combination cell NE-B are so connected that their positive poles are both connected at the same end of the resistance R. The negative pole of the storage battery is attached to the other end of the resistance R, so that the whole current of the storage battery discharges

constantly through R . The latter should be great enough to avoid heating, and to maintain a constant potential between the ends of R . The other terminal of the combination (the negative pole) is then moved along the resistance R till some distance, a , is reached at which the electromotive force of $NE-B$ is exactly balanced by the electromotive force of the storage battery for that fraction of R represented by a . In this case there is no deflection of the galvanometer; at other points the galvanometer will be deflected either to the right or left, according as too much or too little electromotive force is used to balance $NE-B$. The electromotive force of the storage battery is, of course, first calibrated by comparing it with a standard Clark cell, placed where $NE-B$ is.

This method of determining the electromotive force of a cell is deservedly considered one of the most reliable. With non-polarizing cells, it certainly leaves nothing to be desired. But, in investigations of this kind with cells that are easily polarized, accurate results are obtained only by a long number of very tedious approximations, which render the work almost interminable. For it is, of course, impossible to hit the right balance at first, and if the connection is made at any point except the right one, the metallic electrode will receive either a positive or negative charge from the storage battery, and a true reading will be thus made impossible. It is necessary to change the entire solution in B , put in new electrodes at M , drive out the diffused cyanide solution from NE , and so on, until these operations have been repeated perhaps a dozen times. If this is not done the results are very unreliable. With the deflection method, on the other hand, the observations may be made very rapidly, and though there is a tendency for the readings to be a little low unless they are quickly made, still, with a high intercalated resistance, and a delicate reflecting galvanometer, this method seems to be reliable for these quickly polarizing electrodes.

As I have already stated, and as was first pointed out by Ostwald, strictly concordant results are possible only when the electrode is surrounded with a medium already saturated with its ions.

I had intended to verify the results in Table I. with the zero method before publication, but although I had all the apparatus set up for over two years, ready to begin at any time, I was prevented from touching it by the constant pressure of routine work till shortly before the time set for the San Francisco meeting of the Institute, in September, 1899. Meantime Prof. A. von Oettingen, professor of physics in the University of Leipzig, read a very valuable paper on this subject before the Chemical and Metallurgical Society of South Africa, in January and February, 1899. In this paper he gives the results of a large number of determinations which he made of the electromotive force of metals in cyanide solutions by means of Poggendorff's compensation method, or, as I shall call it for brevity, the zero method.

Prof. von Oettingen's results are given in Table II.

The above results were all obtained by the Poggendorff compensation or zero method, the Lippmann capillary electrometer being used as an indicator instead of a galvanometer.

Prof. von Oettingen says of these results :

"The two figures in each column refer to the first and last observations on each metal, the intermediate values being omitted. The time occupied by the change is very variable; copper, for instance, took an hour. When no changes occur, this is indicated by a constant. The changes of potential are not always in the same direction, sometimes decreasing, sometimes increasing. But the direction of the changes in any given metal is always the same."

It will be noticed on examining the table that this last sentence is not correct (unless there should be a typographical error in his table). For gold, silver, copper, cobalt, ferric oxide, and lead peroxide, the highest value for the same metal is sometimes the first and sometimes the second value. In

the case of copper $\frac{M}{100}$ potassium cyanide the results jump from -0.212 volt to $+0.380$ volt,—a difference of 0.592 volt.

Table II.—Potentials of Different Metals in Contact with Potassium Cyanide Solutions at 25° C.
Experiments of Prof. A. von Oettingen, Jour. Chem. and Metallurgical Soc., South Africa, January and February, 1899.

	$\frac{M}{1} \text{ KCN.}$	$\frac{M}{10} \text{ KCN.}$	$\frac{M}{100} \text{ KCN.}$	$\frac{M}{1000} \text{ KCN.}$	$\frac{M}{100} \text{ KCN} + \frac{M}{0.670} \text{ Au.}$
	Volt.	Volt.	Volt.	Volt.	Volt.
Au	+0.340 to +0.306	+0.180 to +0.218	—0.092 to —0.056	—0.414 to —0.474	—0.020 to —0.170
Ag	+0.330 " +0.314	+0.176 const.	—0.020 const.	—0.340 " —0.200	—0.308 to —0.330
Cu	+0.890 " +0.924	—0.680 to +0.648	—0.212 ¹ to +0.380	—0.550 " —0.230	
Hg	+0.162 " +0.200	+0.008 " +0.024	+0.056 const.		
Ni	—0.290 " +0.194	—0.466 " —0.392	—0.550 to —0.488	—0.560	
Co	+0.182 " +0.196	+0.118 " —0.220 ²	—0.168 " —0.240		
Fe	+0.056 " —0.146	+0.034 " —0.012	—0.054 " +0.022	—0.008 to 0.050	
Fe ₂ O ₃	—0.674 " —0.700	—0.796 " —0.720	—0.824 " —0.750		
PbO ₂	+0.160 const.	+0.110 " +0.118	—0.062 " +0.070	—0.006 const.	
Pb	+0.164 const.	+0.128 const.	+0.120 const.	+0.120 "	+0.126 const.
Zn	+0.924 " +0.940	+0.780 to +0.800	+0.560 to +0.604	+0.480 "	

¹ On moving the fluid the potential suddenly rises.

² The potential changed suddenly from —0.121 to +0.118, then remained constant. (Note the discrepancy between —0.230 in the table and —0.121 in the footnote.)

I shall speak of the probable cause of these differences later.¹

In order to make clearer the meaning of Prof. von Oettingen's results, I have plotted them in Fig. IV., as mine are plotted in Fig. II. In the figures, x is made to mark the molecular concentration, $\frac{M}{1}$, $\frac{M}{10}$, $\frac{M}{100}$, $\frac{M}{1000}$; the y axis shows

¹ There are some other potential differences given by Prof. von Oettingen which I include here.

$\frac{\text{Hg}}{\text{Hg}_2\text{SO}_4}$	= -0.99 volts.	(Ostwald),	$\frac{M}{1}$	solutions.
$\frac{\text{Zn}}{\text{ZnSO}_4}$	= +0.524	"	"	"
$\frac{\text{Mg}}{\text{MgSO}_4}$	= +1.243	"	"	" 18° C.
$\frac{\text{Cd}}{\text{CdSO}_4}$	= +0.158	"	"	"
$\frac{\text{Pb}}{\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2}$	= -0.089 volts.	"	"	"
$\frac{\text{Cu}}{\text{CuSO}_4}$	= -0.582	"	"	"
$\frac{\text{Ag}}{\text{Ag}_2\text{SO}_4}$	= -1.024	"	"	"
$\frac{\text{Hg}}{\text{Hg}_2\text{Cl}_2}$	= -0.560	(Ostwald's normal electrode).		

Prof. von Oettingen himself determined the following also (all at 25° C.):

$\frac{\text{Au}}{\text{AuCl (conc)}}$	= -1.64 to 1.42 volts, variable.
$\frac{\text{Au}}{\frac{M}{1} \text{ AuCl}_3}$	= -1.134 volts.
$\frac{\text{Au}}{\text{Aqua regia}}$	= -1.09 volts.
$\frac{\text{Au}}{\text{KCNS (sat.)}}$	= -0.26 to +0.03, very variable.
$\frac{\text{Au}}{\frac{M}{1} \text{ KCNS}}$	= -0.36, variable volt.
$\frac{\text{Au}}{\frac{M}{10} \text{ KCNS}}$	= -0.40 volt.
$\frac{\text{Au}}{\text{KCNS (sat.)}}$	= +0.50 volt.
$\frac{\text{Au}}{\text{K}_2\text{S}}$	= +0.14 volt.
$\frac{\text{Au}}{\text{K}_2\text{S}_7}$	= +0.21 volt.
$\frac{\text{Au}}{\text{Na}_2\text{S}}$	= 0 to 0.136 volt.
$\frac{\text{Ag}}{\text{KCN (sat.)}}$	= +0.536 volt.
$\frac{\text{Cu}}{\text{KCN (sat.)}}$	= +1.154 volts.
$\frac{\text{Zn}}{\text{KCN (sat.)}}$	= +1.196 volts.

the potential in volts. The designation Zinc 1 means that this was the first value obtained with zinc, the designation Zinc 2 the final value, etc. It will be noticed that sometimes the first value is higher than the second and sometimes *vice versa*, but the results are not consistent throughout, sometimes crossing each other.

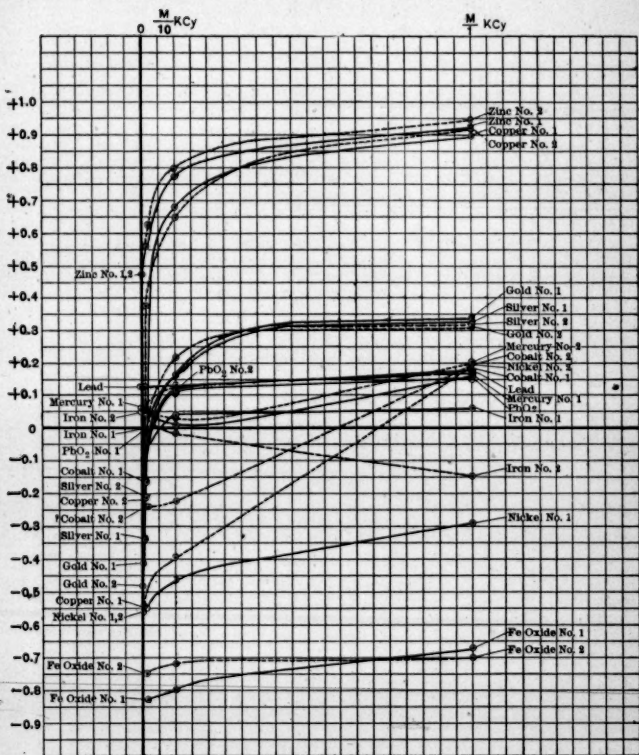
The first curves of each metal, except mercury, approximately follow the logarithmic law (on the assumption that the number of metal ions is inversely proportional to the potassium cyanide concentration). Evidently the curves will cross the X axis at different points, and not usually at a molecular concentration $M = 1$, unless it should accidentally happen that

$$\frac{P}{I} = 1 \text{ for } M = 1.$$

The second curves of zinc, copper, gold, and silver, also approximately follow it. But the second curves of mercury, cobalt, nickel, and iron depart considerably from it. It is possible that these departures are due to polarization effects, as already explained. The irregularities are much more marked than with the deflection method. With that method, provided a sufficiently large resistance is used, the first deflection is the greatest, and is taken as the reading nearest to the truth. The deflection then gradually falls (often quite rapidly, if there is a formation of gas on the face of the electrode); but the electromotive force never rises unless the first effect of the current is to produce a film of gas or insoluble cyanide which puts a stop to the current, either by setting up an opposing electromotive force or by preventing or reducing contact by its resistance. In this case, shaking the solution or jarring the electrode usually gives an increase of the electromotive force by destroying the film in part; but, if the metallic surface is untarnished to begin with, the electromotive force rarely rises again to its first value.

New Method of Plotting Results.—The method of plotting results hitherto used, while it shows very well the near approach of the curve to the true logarithmic curve, has the disadvantage that only three or four values for the tenth ratio

can be plotted. If, however, instead of making $x = \frac{P}{p}$, as we



E.M.F. OF METALS IN CYANIDE - SOLUTIONS.

by Prof. v. Oettingen of Leipzig.
(J. Chem. & Met. Soc. S. A. Feb. 1899.)

$$x - M. \quad y = \pi - 0.058 \log \frac{P}{p} \text{ Volts.}$$

Fig. IV.

have done, we let $x = \log \frac{P}{p}$, and plot the curve $y = 0.058$

$\log \frac{P}{p}$ volts, the curve becomes a straight line passing through the origin at 0. For $x = 0, y = 0$.

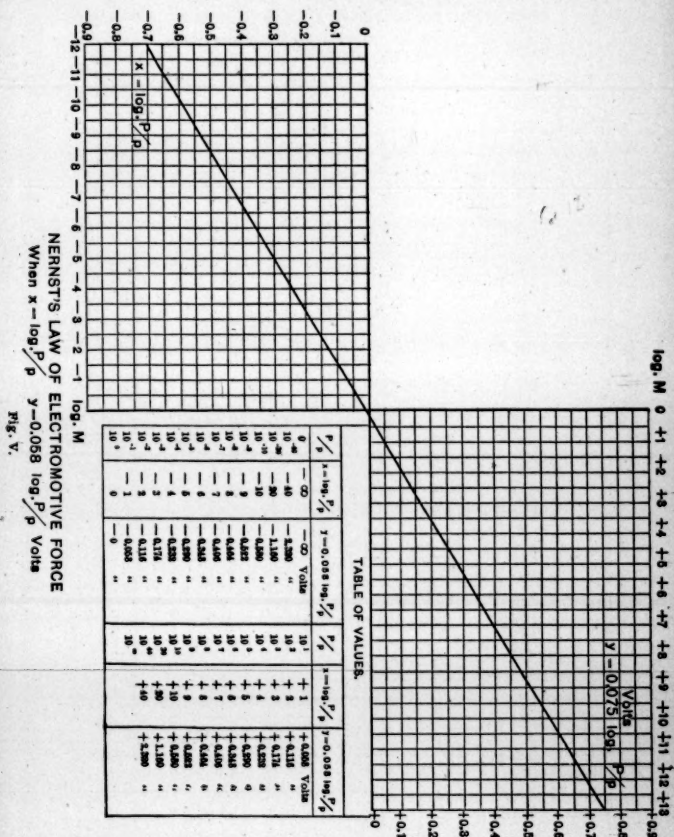
The curve is plotted in Fig. V. for values of $x = \log \frac{P}{p}$ from +13 to -12, which gives voltages from +0.755 to -0.696, and the table shows values from $x = \log \frac{P}{p} =$ minus infinity to 40. It shows that an enormous change in the value $\frac{P}{p}$ is necessary to produce a very moderate change in the voltage. Thus, to produce a change of 2.32 volts, a change in the ratio $\frac{P}{p} = 10^{10}$ (or ten to the fortieth power) is necessary.

In our experiments, of course, we do not know the value of $\frac{P}{p}$, but as a first approximation we may assume it inversely proportional to the molecular concentration $M \times 10^n$.

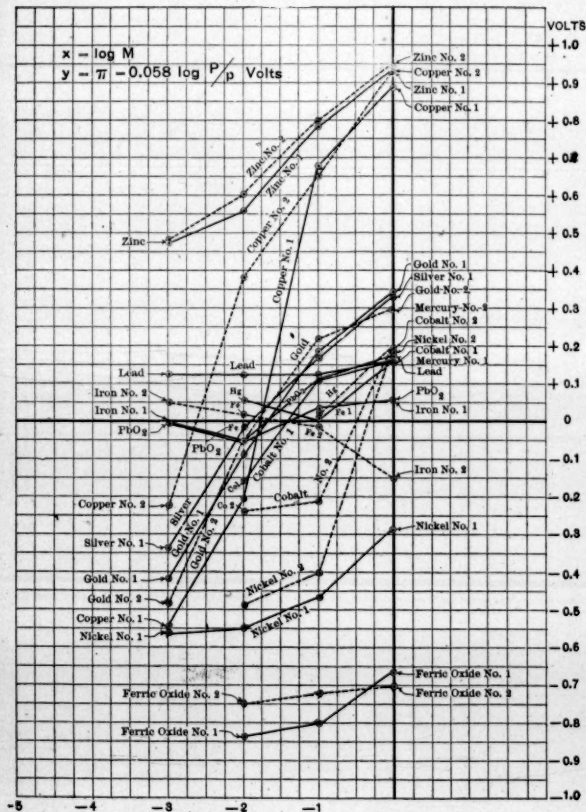
On the axis of x is plotted the logarithm of the molecular concentration expressed in the powers of 10. Thus, $x = \log M = \log 10^{\pm n}$. The y axis gives the electromotive force in volts. For comparison the theoretic formula of Nernst is also given.

If we plot Prof. von Oettigen's results, as in Fig. VI. on this plan, they become at once more intelligible. We see at once that all the curves do not remain straight lines. The zinc follows along very nearly in the theoretic straight line. The copper starts well, but soon falls quite rapidly, due probably to increasing dissociations. The gold and silver approximate fairly well, also, but the rest depart from it considerably.

Comparison of the Deflection and Zero Methods.—Since the results of Prof. von Oettigen were published, I have thought best to try the zero method as well as the deflection method, and to compare the results so far obtained with each other. I have also decided to plot the results by the same method as shown in Fig. V., as it enables us to compare the results over a wider range of dilution than the former method of tabulation would cover.



After the foregoing description and discussion of the various methods employed in this investigation, the reader will be able to study intelligently the tabulated results of the tests herein after stated.



E.M.F. OF METALS IN CYANIDE- SOLUTIONS.

Prof. v. Oettingen of Leipzig. (J. Chem. and Met. Soc. S. A. Feb. 1899.)

Fig. VI.

Results of Experiments.

The following tables show, for the several methods tested, my own results, obtained at different times and by different methods, as well as those of Prof. von Oettingen. In every case each observation was made independently, without regard to the ultimate result of its reduction. But the later readings are more reliable than the earlier, because a certain knack in catching the needle at its maximum position, before the voltage begins to fall, was acquired during the work. The tables give the readings as reduced from the actual observations, without attempted correction; but when any anomaly rendered the observation uncertain this is indicated by a(?). Such was the case particularly in the readings with distilled water (M divided by ∞), which were very uncertain, especially for easily oxidizable metals like zinc and iron.

Experiments with Commercial Sheet Zinc.—Experiments were made at different times with both the zero and the deflection method on the ordinary commercial sheet zinc, such as is actually used in making zinc shavings, for precipitating gold. The results are given in Table III., and those of Prof. von Oettingen have been introduced into the same table, for comparison.

These results are plotted together for comparison in Fig. VII. It will be evident that from $\frac{M}{1}$ to $\frac{M}{100}$, or from 6.5 to 0.065 per cent, the curve nearly follows the theoretic straight line. Curves *a*, *f*, and *g* appear to follow it to $\frac{M}{1,000}$ or 0.0065 per cent, for more dilute solutions beyond that point the curve approximates a horizontal straight line. This, according to the Nernst theory, would mean that the number of zinc ions in such solutions remains nearly constant. In spite of all the irregularities in the curves, the point -3 or $\frac{M}{1,000}$ or 0.0065 per cent potassium cyanide is evidently a critical or inflection-point in the curve.

The results obtained with high dilutions of cyanide and

Table III.—*Electromotive Force of Zinc (Commercial Sheet, Burnished) in Potassium Cyanide.*

Curve.	(a.)	(b.)	(c.)	(d.)	(e.)	(f.)	(g.)
Notebook B1, p.	67	176	177	186	193	Published	Published
Date	Oct. 19, '96	Aug. 30, '99	Aug. 30, '99	Sept. 4, '99	Sept. 8, '99	Feb., '99	Feb., '99
Method	Deflect. ¹	Zero. ²	Deflect. ³	Deflect. ⁴	Deflect.	Zero.	Zero.
Resis. ohms	100,000		100,000	100,000	200,000		
Temperature	22° C.	19° C.	19° C.	19° C.	198° C.	25° C.	25° C.
Observer	Christy	Christy.	Christy.	Christy.	Christy.	Von Oet- tingen.	Von Oet- tingen.
EMF	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
(N.E. = -0.560)							
Concentration							
KCN $\frac{M}{I}$		+0.946		+0.906	+0.914 ⁴	+0.924	+0.940
$\frac{M}{10}$	+0.770	+0.861		+0.815	+0.836 ⁴	+0.780	+0.800
$\frac{M}{100}$	+0.585	+0.772		+0.730	+0.735 ⁴	+0.560	+0.604
$\frac{M}{1,000}$	+0.385	+0.415	+0.386	+0.300	+0.371 ⁵	+0.480	+0.480
$\frac{M}{10,000}$		+0.385(?)	+0.326	+0.270	+0.332		
$\frac{M}{100,000}$		+0.355	+0.320	+0.270(?)	+0.332(?)		
$\frac{M}{1,000,000}$		+0.383(?)	+0.312	+0.282(?)	+0.332(?)		
$\frac{M}{\infty} (= H_2O)$	+0.041(?)	+0.372(?)	+0.256(?)	+0.240(?)	+0.293(?)		
				+0.350(?)			

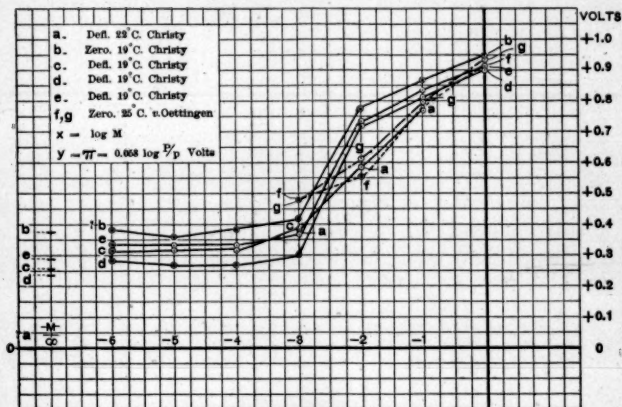
¹ Used same strip of zinc throughout experiments, burnishing each time. Tested from strong to weak solutions.

² Same strip, burnished and tested each time.

³ Same strip, burnished and tested from weak to strong solutions.

⁴ Fine bubbles form on zinc and then voltage falls. Shaking causes bubbles to escape, and voltage rises.

⁵ Below this no gas bubbles visible to naked eye, but voltage falls, and then rises on shaking.



E.M.F. OF ZINC IN KCy. SOLS.

Fig. VII.—On the horizontal (x) axis are laid off the values of $\log M = \log 10^6$; on the vertical (y) axis the actual volts.

with distilled water were very uncertain, probably because of the formation of insoluble films of oxide of zinc and occluded hydrogen, which prevented the accurate reading of the needle.

In my results with the deflection method, I have always taken the highest reliable reading as the most probable result. It was often quite difficult to make sure of the proper reading, as a slight insoluble film of cyanide of copper formed almost instantly, and this lowered the potential almost before a reading could be taken. On agitating the copper so as to bring it into contact with fresh solution, the potential would gradually rise to a maximum, after which, on being left at rest, it would again fall off more gradually. It is possible, also, that the tendency of copper to form cupric, as well as cuprous cyanide, may in part explain the discordant results, such, for instance, as that obtained by Prof. von Oettingen with $\frac{M}{100}$ potassium cyanide solution. He says in a foot-note

Table IV.—*Electromotive Force of Copper (Burnished Sheet) in Potassium Cyanide.*

Curve.	(a.)	(b.)	(c.)	(d.)	(e.)	(f.)	(g.)
Notebook B1, page	68	178	188	189	190	Published	Published
Date	Oct. 20, '96	Aug. 30, '99	Sept. 6, '99	Sept. 6, '99	Sept. 7, '99	Jan., '99	Jan., '99
Method	Deflect.		Deflect.	Zero.	Deflect.	Zero.	Zero.
Resis. ohms	100,000	Zero.	100,000		200,000		
Temperature	23° C.	18° C.	18° C.	18° C.	19° C.	25° C.	25° C.
Observer	Christy.	Christy.	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
(N. E. = -0.560)							
Concentration :							
KCN $\frac{M}{1}$	+0.930	+0.910	+0.905	+0.811(?)	+0.860	+0.924	+0.890
$\frac{M}{10}$	+0.620	+0.731	+0.310	+0.663	+0.660	+0.680	+0.648
$\frac{M}{100}$	+0.370	+0.146	+0.310	+0.356	+0.149	-0.212	+0.380
$\frac{M}{1,000}$	+0.158	-0.104	-0.068	-0.048	-0.151	-0.550	-0.230
$\frac{M}{10,000}$		-0.332	-0.241	-0.230	-0.324		
$\frac{M}{100,000}$		-0.360	-0.299	-0.272	-0.387		
$\frac{M}{1,000,000}$		-0.426	-0.314	-0.282	-0.442		
$\frac{M}{\infty} (= H_2O)$	-0.560(?)	-0.444	-0.328	-0.313	-0.450		

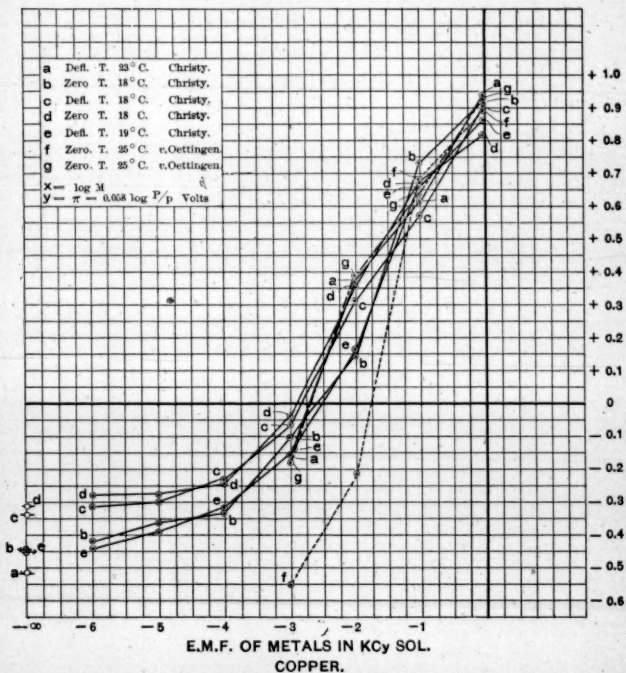


Fig. VIII.—On the horizontal (x) axis are laid off the values of $\log M = 10^x$; on the vertical (y) axis, the actual volts.

concerning this case, "On shaking, the potential suddenly rises from -0.212 to $+0.380$."

The results contained in the above table have all been plotted in Fig. VIII. The mean results of these curves show a tendency to follow the course of a straight line from $\frac{M}{1}$ down to $\frac{M}{1,000}$; or perhaps to $\frac{M}{10,000}$; that is, from 6.5 down to

0.00065 per cent, when it breaks off sharply and runs along flat again, just as the zinc curve did.

On plotting the gold curves, as has been done in Fig. IX., it is evident that the gold follows the logarithmic law fairly well as far as $\frac{M}{100}$ or 0.065 per cent potassium cyanide. A considerable fall of potential occurs, according to my experiments, between $\frac{M}{100}$ and $\frac{M}{1,000}$, or 0.0065 per cent potassium cyanide, indicating an increase of osmotic pressure, probably due to an increasing dissociation of the potassium aurous cyanide. This point seems again a critical point in the curve, which, beyond it, runs off more flatly, indicating an approach to a constant osmotic pressure of the gold ions.

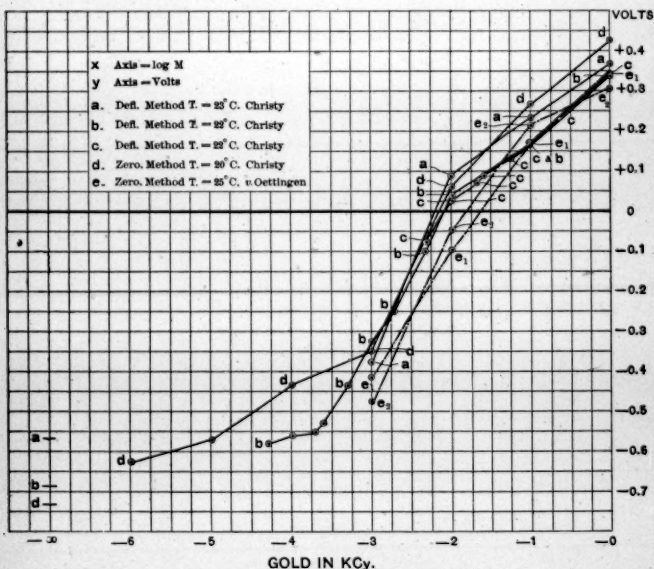


Fig. IX.—On the horizontal (x) axis are laid off the values of $\log M = \log 10^n$; on the vertical (y) axis, the actual volts.

Table V.—*Electromotive Force of Gold in Potassium Cyanide Solutions.*

Curve.	(a.)	(b.)	(c.)	(d.)	(e.)	(f.)
Notebook B1, page	71	86	88	172	Published Feb., '99	Published Feb., '99
Date	Oct. 20, '96	Dec. 12, '96	Dec. 14, '96	Aug. 26, '99	Zero.	Zero.
Method	Deflect.	Deflect.	Deflect.	Zero.	Zero.	Zero.
Resis. ohms	100,000	50,000	50,000			
Temperature	23° C.	22° C.	20° C.	20° C.	25° C.	25° C.
Observer	Christy.	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
(N. E. = -0.560)						
Concentration KCN :						
6.4 M			+0.468			
3.2 M			+0.420			
1.6 M			+0.357			
M $\frac{1}{1}$	+0.366	+0.334	+0.336	+0.418	+0.340	+0.306
M $\frac{1}{2}$			+0.288			
M $\frac{1}{4}$			+0.239			
M $\frac{1}{10}$	+0.233	+0.176	+0.176	+0.264	+0.180	+0.218
M $\frac{1}{20}$			+0.135			
M $\frac{1}{40}$			+0.093			
M $\frac{1}{50}$			+0.073			
M $\frac{1}{100}$	+0.087	+0.045	+0.037	+0.065	-0.092	-0.056

Table V.—*Electromotive Force of Gold in Potassium Cyanide Solutions (Continued).*

Curve.	(a.)	(b.)	(c.)	(d.)	(e.)	(f.)	382
M		—0.099	—0.773				
200		—0.244					
M		—0.326		—0.348	—0.414	—0.474	
500		—0.436					
M		—0.533					
1,000		—0.554					
M		—0.560		—0.439			
2,000		—0.581					
M			—0.567				
10,000			—0.622				
M							
1,000,000							
M	—0.560(?)	—0.698		Sept. 4, '99			
∞ (= H ₂ O)				Deflection			
				—0.724			
				—0.620			
				—0.709			

Christy.

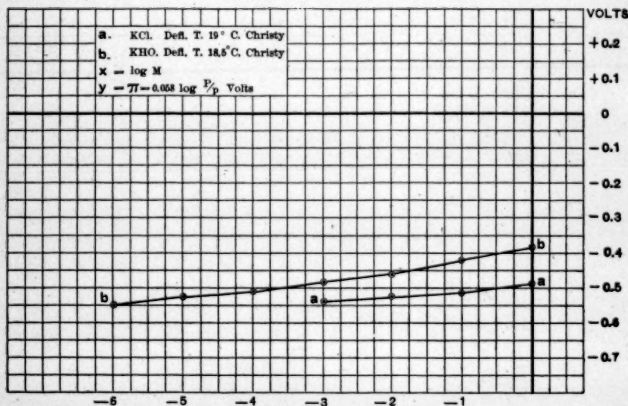
Electromotive Force of Gold in Potassium Chloride and Potassium Hydroxide.

In order to bring out the effect of the potassium cyanide in reducing the osmotic pressure of the gold ions in the solution (according to the Nernst theory), I append the following experiments on the electromotive force of gold in solutions of potassium chloride and potassium hydrate. These results are given in Table VI., and are plotted in Fig. X. It is evident

Table VI.—Electromotive Force of Gold in Potassium Chloride and Potassium Hydroxide.

Curve.	(a).	(b.)
Notebook B1, page	160	159
Date	Aug. 10, '99	Aug. 10, '99
Resistance, ohms	30,000	30,000
Temperature	19° C.	18°.5 C.
Observer	Christy.	Christy.
EMF.	Volt.	Volt.
(N. E. = -0.560)		
Solution	KCl.	KOH.
Concentration :		
M	-0.487	-0.381
$\frac{1}{10}$ M	-0.510	-0.422
$\frac{1}{100}$ M	-0.523	-0.468
$\frac{1}{1,000}$ M	-0.533	-0.486
$\frac{1}{10,000}$ M		-0.505
$\frac{1}{100,000}$ M		-0.526
$\frac{1}{1,000,000}$ M		-0.551

that there is a very much smaller electromotive force in each of these cases. It is particularly low in the case of potassium chloride. According to the Nernst theory, the solution pressure of the gold is the same in each of these solutions ; that is, the pressure with which the gold tends to go into solution



E.M.F. OF GOLD IN KCl AND KHO SOLUTIONS.

Fig. X.—On the horizontal (x) axis are laid off the values of $\log M = \log 10^n$; on the vertical (y) axis, the actual volts.

is exactly the same (at a given temperature), whether the gold is immersed in either potassium cyanide, potassium chloride, or potassium hydrate. But the number of gold ions in each solution, and hence the resulting osmotic pressure, is very different. According to this theory, it is least in potassium cyanide, much greater in potassium hydrate, and greatest of all in potassium chloride. Consequently, the electromotive force varies inversely as p , according to the ratio $\log \frac{P}{p}$.

The curves in both cases run rather flat, indicating an approach to a constant osmotic pressure for high dilutions.

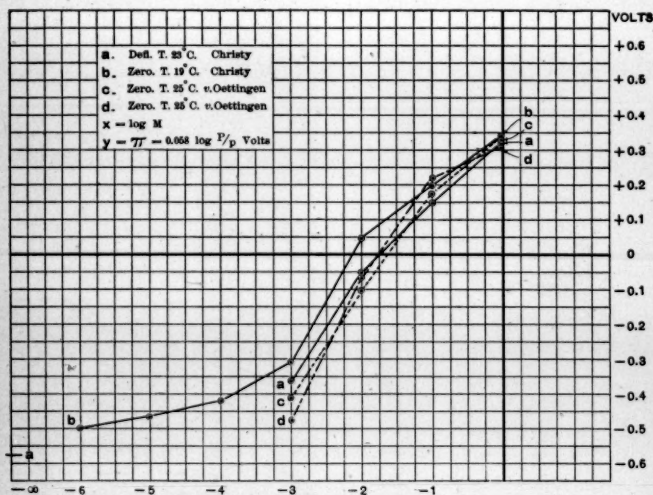
Table VII.—*Electromotive Force of Silver in Potassium Cyanide.*

Curve.	(a.)	(b.)	(c.)	(d.)
Notebook Br, p.	71	170	Published	Published
Date	Oct. 20, '96	Aug. 19, '99	Jan., '99	Jan., '99
Method	Deflect.	Zero.	Zero.	Zero.
Resistance, ohms	100,000			
Temperature	23° C.	19° C.	25° C.	25° C.
Observer	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF	Volt.	Volt.	Volt.	Volt.
(N. E. = -0.560)				
Concentrat'n KCN:				
$\frac{M}{1}$	+0.326	+0.345	+0.340	+0.306
$\frac{M}{10}$	+0.152	+0.194	+0.180	+0.218
$\frac{M}{100}$	-0.054	+0.058	-0.092	-0.156
$\frac{M}{1,000}$	-0.360	-0.308	-0.414	-0.474
$\frac{M}{10,000}$		-0.417		
$\frac{M}{100,000}$		-0.457		
$\frac{M}{1,000,000}$		-0.498		
$\frac{M}{\infty} (= H_2O)$	-0.572			

Table VIII.—*Electromotive Force of Lead in Potassium Cyanide.*

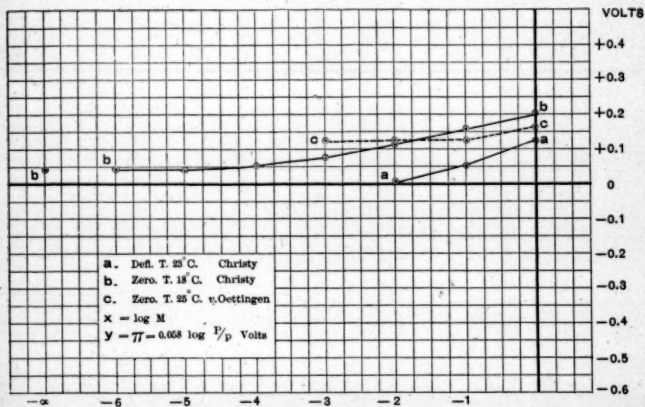
Curve.	(a.)	(b.)	(c.)
Notebook Br, p.	68	183	Published
Date	Oct. 20, '99	Sept. 2, '99	Feb., '99
Method	Deflect.	Zero.	Zero.
Resistance, ohms	100,000		
Temperature	23° C.	18° C.	25° C.
Observer	Christy.	Christy.	Von Oettingen
EMF	Volt.	Volt.	Volt.
(N. E. = -0.56)			
Conc'trat'n KCN:			
$\frac{M}{1}$	+0.125	+0.200	+0.164 const.

Curve.	(a.)	(b.)	(c.)	
$\frac{M}{10}$	+0.050	+0.158	+0.128	"
$\frac{M}{100}$	+0.006	+0.112	+0.120	"
$\frac{M}{1,000}$		+0.070	+0.120	"
$\frac{M}{10,000}$		+0.046		
$\frac{M}{100,000}$		+0.040		
$\frac{M}{1,000,000}$		+0.040		
$\frac{M}{\infty} (= H_2O)$		+0.040		



E.M.F. OF SILVER IN KCy.

Fig. XI.—On the horizontal (x) axis are laid off the values of $\log M = \log 10^n$; on the vertical (y) axis, the actual volts.



E.M.F. OF LEAD IN KCl SOLUTION.

Fig. XII.—On the horizontal (x) axis are laid off the values of $\log M = \log 10^n$; on the vertical (y) axis, the actual volts.

The normal electrode, checked on $\frac{M}{I}$ KCl, showed -0.560 , as it should do.

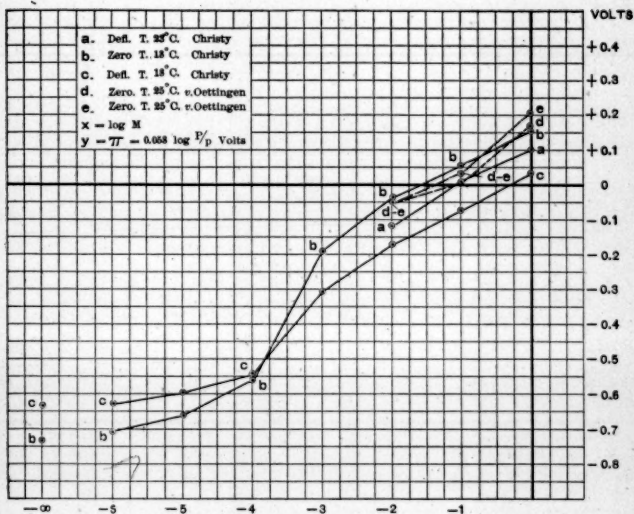
As a check on the foregoing results, I am able to quote the observations of an independent observer, Brandenburg.¹ He conducted a number of experiments with mercury in various depolarizing solutions. Instead, however, of using Ostwald's normal electrode, he used as one electrode mercury covered with sulphate of mercury (instead of the chloride used in Ostwald's). This electrode was then connected, by means of a siphon containing a neutral salt in solution, with a vessel containing mercury covered with the various solutions to be experimented on.

The solutions he experimented on to find their ion destroying-power, or their power to form complex ions with mercury, were: Potassium sulphide, potassium cyanide, potassium thio-cyanate, sodium hyposulphite, potassium ferrocyanide,

¹ Ztschr. phys. Chem., 11, 570, etc.

Table IX.—*Electromotive Force of Mercury in Potassium Cyanide.*

Curve.	(a.)	(b.)	(c.)	(d.)	(e.)
Notebook B ₁ , page	67	184	184		
Date	Oct. 19, '96	Sept. 2, '99	Sept. 2, '99	Published Feb., '99	Published Feb., '99
Method	Deflect.	Zero.	Deflect.	Zero.	Zero.
Resistance, ohms	100,000		100,000		
Temperature	23° C.	18° C.	18° C.	25° C.	25° C.
Observer	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
Volts.	Volts.	Volts.	Volts.	Volts.	Volts.
EMF					
(N.E. = -0.560)					
Concentration KCN :					
M					
$\frac{1}{1}$	+0.091	+0.154	+0.032	+0.162	+0.200
M					
$\frac{10}{10}$	+0.010	+0.147	-0.073	+0.008	+0.024
M					
$\frac{100}{100}$	+0.115	-0.043	-0.176	-0.056	
M		-0.193	-0.309		
$\frac{1,000}{1,000}$		-0.560	-0.545		
M		-0.664	-0.594		
$\frac{10,000}{10,000}$		-0.705	-0.634		
M		-0.735	-0.640		
$\frac{100,000}{100,000}$					
M					
$\frac{1,000,000}{1,000,000}$					
M					
$\frac{\infty}{\infty} = \text{H}_2\text{O}$					



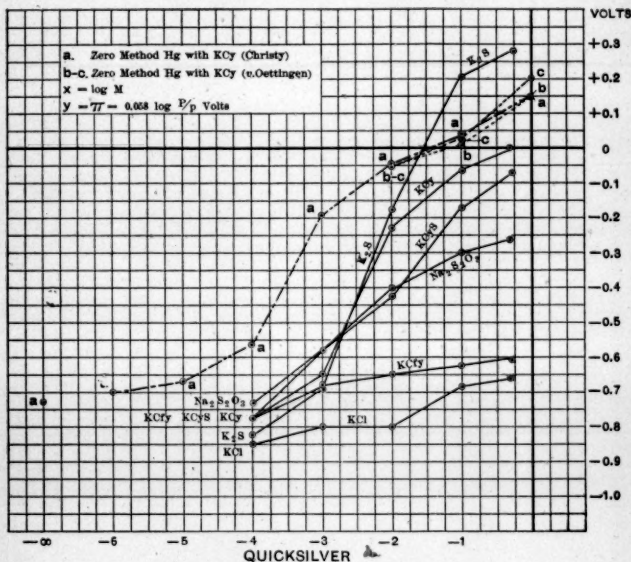
E.M.F. OF MERCURY IN KCy SOLUTION.

Fig. XIII.—On the horizontal (x) axis are laid off the values of $\log M = \log 10^p$; on the vertical (y) axis, the actual volts.

and potassium chloride. As he did not use the same strengths that I have found most convenient, I have had to plot his results, reduce them to zero potential,¹ and interpolate the results for the strengths I have used. The results so obtained are compared with the results obtained by Professor Oettingen and myself with the normal electrode. The results obtained by us for potassium cyanide are higher than Brandenburg's, but show the curves to be of the same general nature. They are shown in Fig. XIV.

¹ On the supposition that $\frac{\text{Hg}}{\text{HgSO}_4}$ has a potential of -0.98 instead of -0.560 for





Mercury Depolarizer/HgSO₄/Hg.

The Results of Brandenburg, (Z.f.Ph.Ch.xl.570. &c.)

Plotted, Interpolated, Replotted and Reduced to 0 Potential, by S.B.Christy.

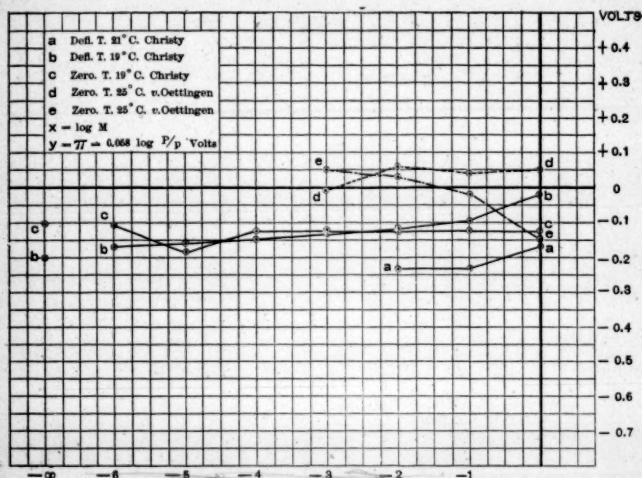
To which are added, for comparison, curves with Normal Electrodes.

Fig. XIV.—On the horizontal (x) axis are laid off the values of $\log M = \log 10^2$; on the vertical (y) axis, the actual volts.

In order to bring out more clearly the nature of the relations existing between the electromotive force of the different metals, I have combined, from the plotted curves of each metal, what appear to be the most probable values for each metal. The results are contained in Table XI.

Table X.—*Electromotive Force of Iron in Potassium Cyanide.*

Curve.	(a.)	(b.)	(c.)	(d.)	(e.)
Notebook Br, page	68	182	180	Published Feb., '99	Published Feb., '99
Date	Oct. 21, '96	Sept. 1, '99	Sept. 1, '99	Zero.	Zero.
Method	Deflect.	Deflect.	Zero.	Zero.	Zero.
Resistance, ohms	100,000	100,000			
Temperature	21° C.	19° C.	19° C.	25° C.	25° C.
Observer	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF	Volt.	Volt.	Volt.	Volt.	Volt.
(N. E. = -0.56)					
Concentration KCN :					
M	-0.169	-0.028	-0.124	+0.56	-0.146
I					
M	-0.236	-0.082	-0.124	+0.34	-0.120
10					
M	-0.236	-0.116	-0.124	+0.054	+0.022
100					
M		-0.131	-0.124	-0.008	+0.050
1,000					
M		-0.146	-0.124		
10,000					
M		-0.160	-0.184		
100,000					
M		-0.160	-0.104		
1,000,000					
M		-0.206	-0.104		
∞ (= H ₂ O)					



E.M.F. OF IRON IN KCy SOLUTION.

Fig. XV.—On the horizontal (x) axis are laid off the values of $\log M = \log 10^n$; on the vertical (y) axis, the actual volts.

Table XI.—*Electromotive Force of Metals in a Solution of Cyanide of Potassium.*

Concentration.		Combination of most probable values.			
M = 10 ⁿ .	Log. 10 ⁿ .	Zinc.	Copper.	Gold.	Silver.
M = 10 ⁰	0	+0.945	+0.930	+0.420	+0.340
M = 10 ⁻¹	-1	+0.870	+0.680	+0.265	+0.195
M = 10 ⁻²	-2	+0.775	+0.430	+0.090	+0.055
M = 10 ⁻³	-3	+0.415	-0.050	-0.340	-0.310
M = 10 ⁻⁴	-4	+0.385	-0.250	-0.450	-0.420
M = 10 ⁻⁵	-5	+0.355	-0.270	-0.565	-0.460
M = 10 ⁻⁶	-6	+0.330	-0.280	-0.620	-0.495
Dist. water	-∞	+0.280	-0.320	-0.720	-0.570
		Lead.	Mercury.	Iron.	
M = 10 ⁰	0	+0.200	+0.150	-0.030	
M = 10 ⁻¹	-1	+0.160	+0.050	-0.090	
M = 10 ⁻²	-2	+0.110	+0.040	-0.120	
M = 10 ⁻³	-3	+0.070	-0.190	-0.130	
M = 10 ⁻⁴	-4	+0.050	-0.590	-0.140	
M = 10 ⁻⁵	-5	+0.040	-0.600	-0.150	
M = 10 ⁻⁶	-6	+0.040	-0.635	-0.160	
Dist. water	-∞	+0.040	-0.640	-0.200	

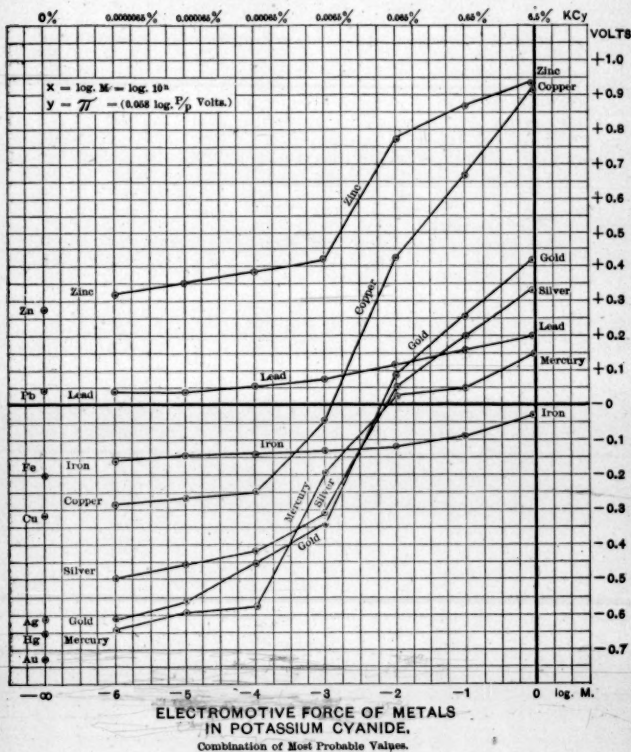


Fig. XVI.

These results have been plotted in Fig. XVI. These curves all show critical points at either $\log M = -2$, -3 , or -4 . Most of them show the greatest amount of inflection at $\log M = -3$. In fact, most of them seem to change in character at this point. According to the Nernst-Ostwald theory,

this would be explained by the assumption that below say $\frac{M}{1,000}$ KCN, the dissociation of the complex ion containing the metal in point is practically complete, so that the osmotic pressure p of the given metallic ions in the dilute solutions becomes practically constant below this point, so that as the ratio $\frac{P}{p}$ is nearly constant, so its logarithm, and hence the voltage becomes also nearly constant, as is shown in the figure.

The curves for lead and iron are very remarkable; at first quite low, they maintain themselves at a higher level than either of the other metals except zinc. This is explainable on the supposition that the values of P for lead and iron are for these metals rather low, but that the values of p reach a nearly constant value sooner than for the other metals, so that the resulting curves flatten earlier.

These curves also show a number of remarkable crossings. Copper, which starts at a voltage slightly less than that of zinc, rapidly falls off, crosses the curve of lead a little below $\log M = -2.5$, and that of iron a little before $\log M = -3.5$, and then remains permanently below these metals. The gold curve crosses the curves of mercury, silver, and iron at just about $\log M = -2.5$. Gold and silver both cross mercury again at about $\log M = -3.5$. Gold finally crosses mercury again at a point beyond $\log M = -6$, and remains permanently below it after that.

It will be observed that the metals change their sequence from that of zinc, copper, gold, silver, lead, mercury, iron, which they possess in a $\frac{M}{1}$, or 6.5 per cent potassium cyanide solution, to the order zinc, lead, iron, copper, silver, mercury, gold, in distilled water, which is the usual electrochemical series in acid solutions quoted by Wilson, except that iron is placed above lead. The determination of iron in my experiments was not entirely satisfactory, by reason, apparently, of the formation of films, and the results are probably too low. Water, also, appears to act like a weak alkali.

All the metals show a critical point somewhere between $\log M = -3$ and -4 , at which dilution they seem to change from the voltage due to the cyanide solution to that which they ordinarily possess.

From a study of these curves there seems to be little support for the so-called "selective affinity" of dilute cyanide solutions for gold and silver, except in the case of copper down to $\log M = -4$, or 0.00065 potassium cyanide. In the case of zinc, lead, iron, and mercury the strong solutions give a better relative voltage in favor of the gold than do the dilute cyanide solutions. But in the case of copper there seems to be a distinct advantage in favor of the gold in dilute solutions down to 0.00065 per cent. Then the curves widen again. These facts will appear from the following table taken from the figure :

Table XII.—Differences in Electromotive Force between Gold and Copper in Solutions of Potassium Cyanide.

Log M = log 10^a .	Value of 10^a .	KCN. Per cent.	Difference be- tween gold and copper. Volts.
0	1 $\div$ 1	6.5	0.51
-1	1 $\div$ 10	0.65	0.42
-2	1 $\div$ 100	0.065	0.32
-3	1 $\div$ 1,000	0.0065	0.30
-4	1 $\div$ 10,000	0.00065	0.20
-5	1 $\div$ 100,000	0.000065	0.30
-6	1 $\div$ 1,000,000	0.0000065	0.34
$-\infty$	1 $\div$ Infinity (H_2O)	0.0	0.40

It should be remarked that if we had an independent method of determining the number of metallic ions in cyanide solutions, and were thus able to plot the electromotive force in terms of the actual ionic concentration instead of the molecular concentration, we should probably reach a more perfect agreement with the logarithmic law than in the curves here shown. Nevertheless, even as it is, a general agreement is certainly evident.

Relation between the Strength of Cyanide Solutions and Their Dissolving Power.

It has already been shown by Maclaurin¹ that the dissolving power of a cyanide solution saturated with oxygen, increases with its strength until a strength of 5 or 10 per cent is reached, and diminishes again as the strength in cyanide increases beyond that point. But, so far as I am aware, no one has proposed the question: "At what point of dilution does the cyanide solution cease to act on the gold?"

According to the Nernst theory, gold should cease to dissolve in cyanide solutions, provided no force acts except its own solution pressure, at the point at which its electromotive force is zero, for then its solution pressure will be just balanced by the osmotic pressure of the ions already in solution. At this point (provided no other force acts) the solution of the gold should cease.

It seemed interesting to ascertain if there was such a point. In order to do so it was necessary to expose the gold to the cyanide solution, in the presence of air, under circumstances most favorable for rapid solution. Hence I devised a rotating apparatus, consisting of three pairs of rollers, driven by a small Pelton water motor, on which a couple of 2.5 liter bottles, such as are used for holding nitric acid, could be laid and rotated about their long axes. The number of revolutions of the middle axis being recorded, the distance traveled was known. This precaution was taken to be able to allow for the irregularities of the motor.

Standard strips of fine gold were prepared by repeated precipitation with sulphurous acid from a diluted chloride solution. These were rolled out thin and cut to a standard size of 2 in. by $\frac{1}{4}$ in. They weighed from 250 to 330 milligrams, according to their thickness. The strips were boiled in sulphuric and muriatic acids, washed, and ignited before use. The first set of experiments was undertaken with 2 liters of solution and 0.5 liter of air, the bottles being stoppered. The weighed gold strips were then added, the bottles were rotated for twenty-four hours, and the strips were then washed and

¹ J. Chem. Soc., 63, 731.

dried and weighed again. The number of rotations made in twenty-four hours ranged from 4,000 to 24,000, and as the interior diameter of the bottles was 4.5 inches, the distance traveled in this time by the gold strip was from 1 to 6 miles. It was impossible to get a uniform rotation rate, owing to constant changes in the water supply. But so long as the solution was kept gently agitated these variations did not seem to have any appreciable effect on the result.¹

Table XIII. shows the results of these experiments. The first pair were undertaken with distilled water, to see if there was any loss due to erosion. The apparent loss of 0.01 milligram was almost at the limit of accuracy of the balance, but seemed to show the possibility of a slight loss due to that cause. It will be observed that up to $\frac{M}{2,000}$, or 0.00325 per cent, the gold loss is merely nominal, never more than 0.29 milligram, often zero, and the results vary in the most irregular manner. No. 18, with $\frac{M}{10,000}$, or 0.00065 per cent, gave a loss of zero, and No. 20, with $\frac{M}{4,000}$, or 0.0016 per cent, only 0.08 milligram. It is believed that these smaller losses below $\frac{M}{4,000}$ were chiefly mechanical. It was noted that while most of the bottles used were perfectly smooth inside, some seemed to have small sharp grains of sand, or slivers of glass, projecting above the smooth inner surface. In many cases it was impossible to detect these without breaking the bottles. The loss in No. 12, which was not rotated, cannot be set down to this cause. The explanation in this case, and perhaps in some others, may have been an imperfect mixing of the solution. The solutions were made up by adding the proper volume of strong solution to the proper amount of distilled water. In case the mixture of the solutions was not thoroughly made before the gold strip was added, the gold would at first lie in a layer of stronger solution that might have a slight solvent

¹ In making these solubility experiments I was aided by my former assistant, now Assistant Professor, E. A. Hersam. I wish also to acknowledge the aid of my present assistant, Mr. Geo. E. Young, in the preparation of the standard solutions used in these experiments, and of the illustrations.

Table XIII.—Solubility of Gold in Cyanide of Varying Strength.

In twenty-four hours. Gold strips, standard size. Fine gold, 2 in. $\times \frac{1}{4}$ in. Weight, 250 to 330 mg. $2\frac{1}{2}$ liter bottles, $4\frac{1}{2}$ in. in diameter, making 4,000 to 24,000 revolutions in twenty-four hours, and containing 2 liters cyanide solution and $\frac{1}{2}$ liter air.

No.	Strength of cyanide.	KCN. Per cent.	Revolutions in 24 hours.	Loss gold in 24 hours. Milligrams.	Remarks.
1	$\frac{M}{\infty} = (H_2O)$		24,461	0.01	
2	$\frac{M}{\infty} = (H_2O)$		13,595	0.01	New strip
3	$\frac{M}{100,000}$	0.000065	15,403	0.01	
4	$\frac{M}{100,000}$	0.000065	10,344	0.008	$\frac{24}{46}$ of 0.2 milligram, the loss in 46 hours
5	$\frac{M}{60,000}$	0.000109	23,750	0.00	
6	$\frac{M}{50,000}$	0.00013	14,430	0.00	
7	$\frac{M}{50,000}$	0.00013	11,315	0.06	
8	$\frac{M}{40,000}$	0.00016	7,920	0.02	
9	$\frac{M}{40,000}$	0.00016	8,490	0.11	
10	$\frac{M}{40,000}$	0.00016	10,180	0.19	
11	$\frac{M}{30,000}$	0.000216	14,850	0.02	
12	$\frac{M}{30,000}$	0.000216	Not rotated	0.11	
13	$\frac{M}{30,000}$	0.000216	8,030	0.29	
14	$\frac{M}{20,000}$	0.000325	6,490	0.20	
15	$\frac{M}{20,000}$	0.000325	17,746	0.01	$\frac{24}{45}$ of loss in 45 hours
16	$\frac{M}{20,000}$	0.000325	17,746	0.025	Same as above

No.	Strength of cyanide.	KCN. Per cent.	Revolutions in 24 hours.	Loss gold in 24 hours. Milligrams.	Remarks.
17	$\frac{M}{10,000}$	0.00065	9,780	0.08	Treated 24 hrs.
18	$\frac{M}{10,000}$	0.00065	9,780	0.00	Duplicate of No. 17
Total loss, Nos. 3 to 18, inclusive				1.133	Average loss, 0.07 mg.
19	$\frac{M}{4,000}$	0.0016	14,423	0.26	} Mean loss, 0.17 mg.
20	$\frac{M}{4,000}$	0.0016	14,423	0.08	
21	$\frac{M}{2,000}$	0.00325	14,423	9.68	
22	$\frac{M}{1,000}$	0.0065	4,260	24.86	} Mean of two, 23.03 mg.
23	$\frac{M}{1,000}$	0.0065	4,260	21.21	
24	$\frac{M}{500}$	0.013	5,790	81.74	} Mean of two, 84.60 mg.
25	$\frac{M}{500}$	0.013	5,790	87.48	
26	$\frac{M}{100}$	0.065	5,270	143.64	} Mean of two, 146.91 mg.
27	$\frac{M}{100}$	0.065	5,270	150.18	

effect until the dilution was effected by rotation. The fact that the mean loss up to $\frac{M}{10,000}$ is only 0.07 milligram; that even at $\frac{M}{10,000}$ (Experiment No. 18), no loss, and in No. 20 a loss of only 0.08 milligram was obtained, renders it extremely probable that the solution loss up to $\frac{M}{10,000}$, or 0.00065 per cent, is absolutely nil. This much is certain: These experiments demonstrate that for all practical purposes the cyanide of potassium solution ceases to act at a strength below 0.001 per cent.

Going to higher strengths we find a sudden jump at $\frac{M}{2,000}$;

here the loss has risen to 9.68 milligram, and beyond this it rapidly increases, the strips in the $\frac{M}{100}$, or 0.065 per cent solution being eaten through in twenty-four hours.

The next set of experiments was devised to show the effect of a smaller volume of cyanide solution and an unlimited supply of air. The same bottles as before were used, but they contained only 500 cc. of solution, and were left open to the air so that the latter was free to enter. The results, as shown in Table XIV., are in general the same as before. No appreciable loss occurs up to $\frac{M}{2,000}$, but at that point, and for greater strengths, the loss rapidly increases, finally rising a little higher than before. In experiments Nos. 4 and 6 the entire solution was filtered and the washed filter was scorified and cupelled. In No. 4, where the gold-loss was 0.07, none was found. In No. 6 (the loss being 0.23 milligram), 0.02 milligram of abraded gold was found. Whether the rest was fine enough to pass the filter or was dissolved before the strong solution was diluted, is a conjecture.

The next experiments were made without agitation and in the following manner: The gold strips were suspended in perforated glass tubes just below the surface of the solution, so that although the solution was at rest, circulation by convection was possible. The volume of the solution was 250 cc. The time of action was in each case forty-eight hours. The losses are given in Table XV.; they are somewhat smaller than before, and again negligible below $\frac{M}{1,000}$. In this case

$\frac{M}{2,000}$ was not determined. The advantage of the position near the surface near the air is well shown in comparing Nos. 5 and 8. When the gold was suspended near the surface of a $\frac{M}{400}$ solution, the loss was 21.44 milligrams in forty-eight hours, or nearly 0.5 milligram per hour; when the strip was put at the bottom of the same volume of a similar solution, the total loss in the same time was only 8.70 milligram, or hardly one-third as much.

Table XIV.—Solubility of Gold in Potassium Cyanide of Varying Strengths in Twenty-Four Hours.

Standard fine gold strips, 2 in. $\times$ $\frac{1}{4}$ in. Weight, 250 to 330 mg. 2½-liter bottles, 4½ in. diameter, making 4,000 to 24,000 revolutions in twenty-four hours. Half a liter cyanide solution, 2 liters air. Freely open to air.

No.	Strength of cyanide.	KCN. Per cent.	Revolutions in 24 hours.	Gold loss in 24 hours. Milligrams.
1	$\frac{M}{\infty}$ (= H ₂ O)		5,110	0.01
2	$\frac{M}{\infty}$ (= H ₂ O)		5,110	0.00
3	$\frac{M}{12,800}$	0.0005	8,440	0.43 (!)
4	$\frac{M}{12,800}$	0.0005	6,600	0.07 ¹
5	$\frac{M}{6,400}$	0.001	8,440	0.19
6	$\frac{M}{6,400}$	0.001	6,600	0.23 ¹
7	$\frac{M}{4,000}$	0.0016	6,790	0.16
8	$\frac{M}{3,200}$	0.002	5,450	0.44
9	$\frac{M}{2,000}$	0.00325	6,790	1.77
10	$\frac{M}{1,600}$	0.004	5,450	4.29
11	$\frac{M}{800}$	0.008	5,540	48.43
12	$\frac{M}{400}$	0.016	5,540	74.96
13	$\frac{M}{200}$	0.0325	28,230	150.54
14	$\frac{M}{100}$	0.065	28,230	168.12

¹ In order to see whether or not these losses might not be due in part, or wholly, to abrasion, the solution was filtered and the filter scorified and cupelled. No gold was found in the filter.

² This solution was also treated as above, and 0.02 milligram of abraded gold was found.

Table XV.—Solubility of Gold in Potassium Cyanide of Varying Strength in Forty-Eight Hours. At Rest.

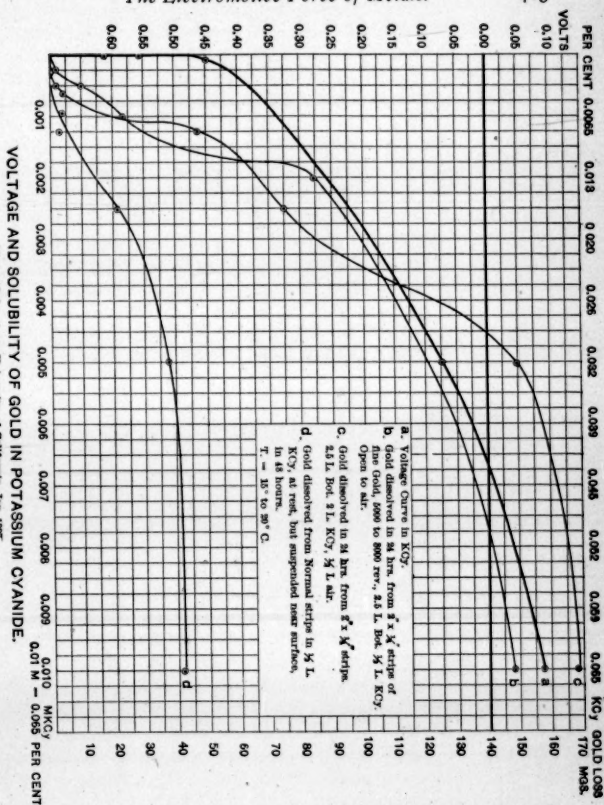
Standard fine gold strips 2 in. $\times$ $\frac{1}{4}$ in. Weight, 250 to 330 milligrams. Suspended in open glass tubes, near surface, of 250 cc. Cyanide solution at rest, but so that convection currents were possible.

No.	Strength of cyanide.	KCN. Per cent.	Gold loss in 48 hours. Milligrams.
1	$\frac{M}{100,000}$	0.000065	0.00
2	$\frac{M}{10,000}$	0.00065	0.06
3	$\frac{M}{1,000}$	0.0065	4.33
4	$\frac{M}{800}$	0.008	3. 8
5	$\frac{M}{400}$	0.016	21.44 ¹
6	$\frac{M}{200}$	0.0325	57
7	$\frac{M}{100}$	0.065	42.79

All these results have been plotted together with the voltage of the gold in curves, *a*, *b*, *c*, and *d* in Fig. XVII. According to the voltage curve the voltage becomes zero for a cyanide solution of 0.00675 M, or about 0.044 per cent, and it is a curious fact that this is very near the limit of strength that practice has so far justified. Nevertheless, solutions as low as 0.01 per cent, and even less, have been employed in practice, and my experiments show that the solution acts perceptibly down as low as $\frac{M}{2,000}$, or 0.00325 per cent, and perhaps to $\frac{M}{4,000}$, or 0.0016 per cent potassium cyanide.

An Apparent Contradiction.—Although it will be seen that the solubility curves follow very closely the voltage curve, the fact that action does not cease for the zero of potential of gold in potassium cyanide solution seems to contradict the Nernst

¹ 8. A similar experiment with same conditions as to strength and volume of solution as No. 5, only that the strip of gold rested at the bottom of the vessel, gave a gold loss of only 8.7 milligrams.



VOLTAGE AND SOLUBILITY OF GOLD IN POTASSIUM CYANIDE.

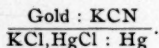
Mining Laboratory, University of California, Jan. 1897.

FIG. XVII.—The values of M KCN on the lower margin, and the corresponding percentages of KCN at the top, belong to each fourth vertical line (1, 2, to the fourth, eighth, twelfth line, etc.) of subdivision. These lines should have been made heavier in the engraving.

law. But this contradiction is only apparent and not real. It is part of the new theory that (except the infinitesimal amounts necessary to produce the state of static tension) ions cannot come into existence or disappear except in pairs. That is, for every ion with a positive charge of electricity

there must be one with an equal negative charge. Hence, when a positive ion appears another positive ion must disappear, or else a negative one must also appear simultaneously. (In the case of ions with varying valency, an ion having a double or triple valency is, of course, equivalent to two or three oppositely electrified univalent ions.)

For instance, in my experiments for determining the electromotive force of gold in potassium cyanide solution against the normal electrode, the couple is composed of



When the gold dissolves, the positive gold ions travel from the gold with their positive charge, and in order that the solution may continue, a similar flow of positive ions must continue by means of potassium ions through the solution to the mercury. The potassium ions finally drive out some of the mercury ions which precipitate into the mercury forming the electrode, at the same time giving up their charge of positive electricity to it. Simultaneously there is a corresponding flow of negative ions in the opposite direction. Thus; first chlorine and then cyanogen move in the opposite direction to meet the gold, and the latter forms with the cyanogen the complex negative ion $(\text{Au}(\text{CN})_2)(-)$. Thus: $\text{Au}(+) + \text{CN}(-) + \text{CN}(-) = (\text{Au}(\text{CN})_2)(-)$.

The action of this couple will go on so long as the electromotive force of the combination is greater than zero, and, as we have seen in my experiments, long after the electromotive force of the gold in the dilute cyanide solution has become zero. For the tendency of the mercury ions to discharge into the mercury electrode, can only affect its purpose and cause a current by the simultaneous solution of the gold. That is, the tendency of the positively electrified ions of mercury to discharge themselves can cause the gold to dissolve long after its own electromotive force has ceased.

The Electromotive Force of the Oxygen of the Air the Sufficient Cause of the Solution of Gold in Cyanide Solutions.

We have another substance at hand with a great tendency

to form negative ions. This is the oxygen of the air. In the presence of water, the molecule of oxygen, O_2 , tends to assume the ionic state, combining with water to form four negatively electrified ions, thus: $O_2(\pm) + 2H_2O(\pm) = 4(OH)(-)$. Or, as has been suggested by Traube, when metals dissolve in the presence of oxygen, a molecule of the latter combines directly with 2 atoms of potentially nascent hydrogen, thus: $O_2 + 2H = H_2O_2$. Later, the peroxide of hydrogen dissociates into two negative hydroxyl ions, which, entering the solution with their negative charges of electricity, tend to produce a current in the same direction as the positively electrified mercury ions do when they leave the solution. That is, oxygen can play the same part in causing the solution of the gold as the mercury ions did in the normal electrode above cited.

The controlling importance of an abundant supply of oxygen is well shown by the curves in Fig. XVII. In curve *c*, although there is only one-fourth as much cyanide present as in curve *b*, the amount of gold dissolved is greater, except for the very dilute solutions. The evident reason that the aeration is greater. The cyanide supply being ample in both cases, the oxygen supply determines the rate of solubility. For dilute solutions, the amount of dissolved oxygen being sufficient in *b*, the greater volume of cyanide is the determining factor, and the amount dissolved in *b* is in this case greater than in *c*.

Interesting confirmation of these views is found in MacLaurin's experiments on the solubility of gold in a solution of cyanide of potassium saturated with oxygen.¹ He conducted two sets of experiments with gold strips in solutions of different strengths. The first set was left at rest for three hours, the second set was agitated. The losses are given in the following table:

Table XVI.—MacLaurin's Table of Losses of Gold in Potassium Cyanide Saturated with Oxygen.

At rest in solution saturated with oxygen. Time, three hours.								
KCN, per cent	1	5	10	20	30	40	50	
Gold loss, mg. ²	8.45	13.55	15.40	11.15	8.55	5.8	5.05	

¹ J. Chem. Soc., 63, 713.

² Curve A, Fig. XVIII.

Agitated for two hours in solution saturated with oxygen.

KCN, per cent	1	4.9	9.4	19.93	29.5	39	10.8
Gold loss, mg. ¹	18.7	47.2	39.1	31.4	21.1	14.2	10.8

Maclaurin deems the results in the second table more reliable than those in the first. In both it will be seen that there is a rapid increase of the dissolving power up to about 5 or 10 per cent potassium cyanide, then it gradually falls off till at 50 per cent the solubility of the gold is less than at 1 per cent.

The importance of the remarkable relation thus discovered by Maclaurin has, I think, never before been appreciated. Is it not a little remarkable that the strong cyanide solution should dissolve less gold than a weak one, while the electromotive force of the gold goes on steadily increasing?

But in the light of the new theory the reason is not far to seek, for at no time does the electromotive force of the gold rise high enough to displace without external aid any other positive ions, such as those of the potassium in the cyanide or the hydrogen in the water, and unless this is done the gold ions cannot continue to form, nor the gold to dissolve. For this reason (as Maclaurin, myself, and others have shown), in the absence of oxygen or some equivalent agency, gold does not dissolve in cyanide solutions. In other words, unless some negative ion like $(OH)(-)$, $(Cl)(-)$, or $(Br)(-)$ is added, or some other positive ion as $(K)(+)$, etc., is removed by some external source of energy, the action cannot go on. Ordinarily, the oxygen of the air furnishes this energy; as we have seen above, it dissolves in the solution and furnishes the negative ions necessary to cause the solution of the gold.

Again, Maclaurin has found the key to the anomalous action of strong cyanide solutions. It is in the fact which he demonstrated, that oxygen is less soluble in strong than in weak cyanide solutions. The following results for the solubility-coefficient of oxygen in potassium cyanide are plotted from the curves by interpolation:

¹ Curve B, Fig. XVIII.

Table XVII.—*Solubility of Oxygen in Solutions of Potassium Cyanide at 18° C. (MacLaurin.)*

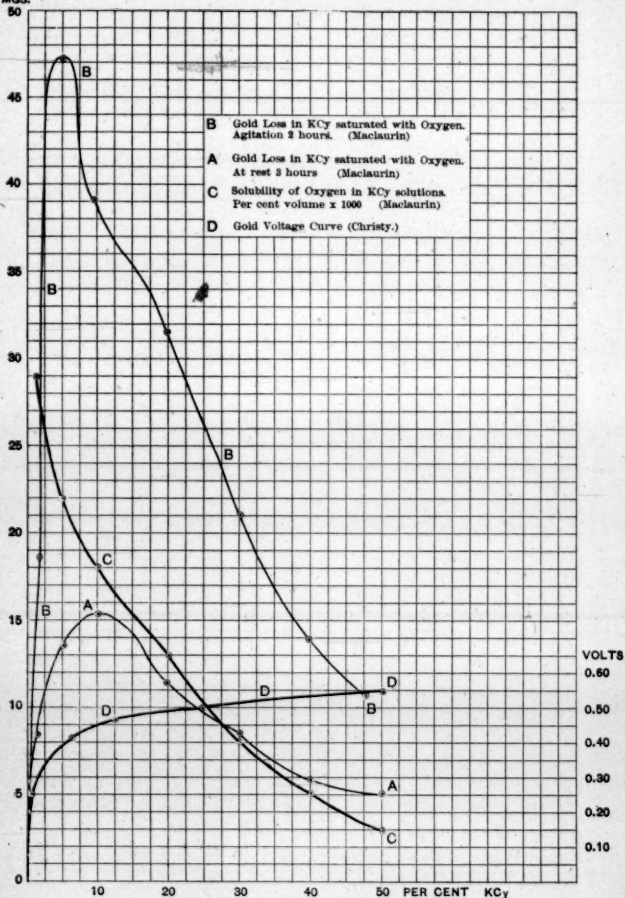
Strength KCN, per cent	1	5	10	20	30	40	50
Solubility, per cent	0.0295	0.0235	0.019	0.014	0.0103		
Solubility, per cent ¹	0.0290	0.022	0.018	0.013	0.008	0.005	0.003

I have replotted the results of the above experiments of MacLaurin so as to make them more comparable with my own results. I have replotted both the gold losses of MacLaurin and the second of his oxygen solubility coefficients in Fig. XVIII, and I have also added the voltage curve for gold from my own experiments.

It is plain now, for the first time, why there should be a maximum solubility somewhere between 5 and 10 per cent. There are two causes at work tending to dissolve the gold. First, the electromotive force of the gold itself, which alone is insufficient for the purpose; and second, that of the hydroxyl ions. If we suppose the latter proportional to the solubility of the oxygen, we see that the two forces operating to cause the solution of the gold tend to increase in inverse relation. Further, that the electromotive force of the gold rises very rapidly till it gets to between 5 and 10 per cent, and then rises very slowly after that, so that it has little effect on the solubility beyond that point. The solubility of the oxygen (and, as we have assumed, of the hydroxyl ions) is a maximum for pure water, and sinks as the gold voltage rises. It is at between 5 and 10 per cent that these two factors give their maximum effect. Beyond that point, the solubility curves of the solution for oxygen and for gold run along nearly parallel.

Neither of these two factors alone is able to account for the maximum point in the solubility curve. If the presence of oxygen were the only cause, the maximum solubility would be with dilute solutions. If it were alone due to the electromotive force of the gold, it would be greatest in strong solutions. As both act together, the maximum effect lies between these extremes.

¹ Curve C, Fig. XVIII.

GOLD LOSS
MGS.

SOLUBILITY OF GOLD AND OXYGEN IN KCy,

From experiments of Maclaurin. (J. Chem. Soc., 1893, pg. 724.)
 Replotted, and Gold Voltage - Curve Added.

Fig. XVIII.

As far as I am aware, this inverse relation between the electromotive force of gold and that of oxygen in cyanide solutions of varying strength, as a controlling factor in determining the solubility of gold in such solutions, has never been brought out before. In a certain sense it is a turning-point in this discussion, and hence merits a little close attention.

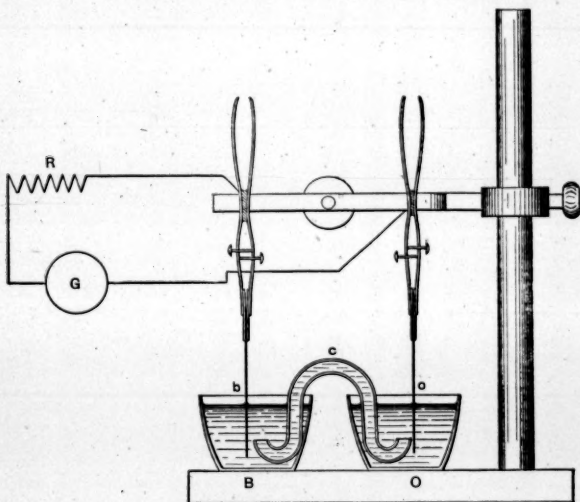
The ionizing tendency of oxygen has been measured by a cell containing a platinum electrode made absorbent for oxygen by coating it with platinum sponge.¹ When this is immersed in oxygen at atmospheric pressure, and the end of the wire is immersed in $\frac{M}{I}$ sulphuric acid, and the latter is connected with the normal electrode, the mercury dissolves, and a positive current flows through the solution from the mercury to the platinum with a potential of +0.75 volt.

This current moves in the opposite direction to that due to the electromotive force of the mercury, *viz.*: -0.560 volt; consequently, the electromotive force of the oxygen at atmospheric pressure in contact with platinum sponge in $\frac{M}{I}$ sulphuric acid is equal to the sum of these, or 1.31 volts. It is negative, or -1.31 volts, since negative ions are produced, and the solution is negatively electrified by them.

If the above determination is correct, it follows that if, instead of the normal electrode in the above combination, we place a vessel containing a gold electrode and a solution of cyanide of potassium so weak that the potential of the gold is not merely zero, but as low as that of the mercury, *viz.*, -0.560, it is plain that a similar voltage of +0.75 should exist; but in this case the gold would dissolve instead of the mercury, and the positive current would flow through the solution from the gold to the platinum, as before. In this case it would be, of course, necessary to interpose an $\frac{M}{I}$ solution of K_2SO_4 , KCl , or some other neutral salt, between H_2SO_4 and the KCN , to prevent their direct action with each other from interfering with the mere transfer of electromotive forces at the end of the line which we wish to effect.

¹ LeBlanc: "Electrochemistry," p. 221.

Now gold does not absorb and ionize oxygen as readily as platinum does, but it acts similarly, though to a much less extent. In order to test the correctness of these views, I took



APPARATUS FOR SHOWING THE
LOCAL ELECTROLYTIC ACTION
INVOLVED IN THE
SOLUTION OF GOLD IN
AERATED CYANIDE SOLUTION
Fig. XIX.

two small porcelain cups, B and O, Fig. XIX., in which were immersed the two electrodes *b* and *o*. These were gold strips held in platinum-tipped forceps, connected in series with a reflecting galvanometer G of 3,000 ohms resistance, including that of the cell, and a resistance R of 30,000 ohms. The solution in either vessel is connected electrically by the liquid in the siphon C.

It is very difficult to prepare, and impossible to keep, a cyanide solution entirely free from oxygen, unless it is hermetic-

ally sealed. But the following method was selected as giving an approximation to it. A liter of distilled water was boiled under a filter-pump, and when most of the dissolved oxygen had been removed cyanide of potassium was added, and the boiling was continued a few minutes to drive out the air absorbed during the solution of the cyanide. A cork was provided with two tubes like those of an ordinary wash-bottle, and after inserting the long tube below the surface, a layer of paraffine oil was floated on to the surface to exclude the air. The tip of the discharge-tube was kept closed by a cork when not in use. It was easy, by blowing in through the short tube above the surface of the oil, to discharge any required amount of the solution as required, but of course each time this was done a small amount of air entered the solution. After cooling, the liquid was titrated and found to contain 0.62 per cent potassium cyanide. A similar 0.621 per cent potassium cyanide solution was prepared and nearly saturated with oxygen. Through the galvanometer G and the resistance R, a Clark cell gave a deflection of 7 scale divisions. In vessel B were placed 12 cc. of boiled 0.62 per cent potassium cyanide solution, and in O an equal volume of 0.621 per cent potassium cyanide solution containing oxygen. On immersing the gold strips, the strip in B became negative, that is, the positive current flowed from B through the solution to O, with an electromotive force = +0.02 volt. When the liquid in both B and O was covered with paraffine oil to exclude the air, the electromotive force rose to +0.108 volt. On gently shaking electrode o, the electromotive force rose to +0.185 volt, on gently shaking B it fell to +0.08 volt (owing to absorbed oxygen). On cutting out the 30,000 ohms resistance, leaving that of the galvanometer (3,000 ohms), the deflection rose to 6.5 scale divisions, coming back again on inserting the resistance R to 0.6 scale divisions, or +0.12 volt. This gradually fell to 0.2 scale division, or +0.04 volt, where it remained for two hours. At the end of that time the resistance was cut out and the deflection rose to 2.5 scale divisions, then, on shaking, to 12 divisions, and then sank again to 2.7, where it remained fairly steady for two hours longer. At the end of this time, four hours in all, the electrodes were removed and

cleaned with gasoline and ether from the oil and solution, and it was found that the electrodes had lost weight as follows :

b lost 1.28 mg.

o lost 1.73 mg.

The solutions contained in the vessels B and O and in the siphon C were also assayed with the following results :

B contained 1.25 milligrams, O contained 1.68 milligrams, and C contained 0.06 milligram of gold.

The total loss of the electrodes was 3.01 milligrams, and that found was 2.99 milligrams. The difference of 0.2 milligram was probably lost in the washings of the electrodes which were not saved.

This experiment, corroborated by many others, shows clearly that the positive current flows from the deoxygenated to the oxygenated cyanide, just as theory would indicate. The fact that more gold has dissolved in the oxygenated than in the deoxygenated cyanide, does not militate against the indication of the galvanometer.

The solution of the gold in the vessel O is evidently due to the well-known phenomenon of "local action." The current that flows through the siphon has to overcome a resistance of from 3,000 to 33,000 ohms, while local action can go on in the vessel O wherever an OH(—) ion comes in contact with gold and potassium cyanide. Here it forms a "short circuit," and it completes itself on the gold strip *o* at any point free from oxygen, without having to pass through the entire external circuit.

It might be objected that the fact that 1.73 milligrams of gold had dissolved in O as against 1.28 in B only went to prove that some oxygen had been contained in B, though less than in O, and that the solution in each had been simply in proportion to the oxygen present. But this does not account for the absolute verdict of the galvanometer, which shows that the positive current flows during the entire experiment from strip *b* through the solution to the strip *o*. The only explanation that remains is the one which I have suggested. There is no doubt that considerable local action went on in cell O. That this was the case is also evidenced by the fact that the action was more uniformly distributed over the surface of *b*,

while the strip *o* was not uniformly acted on, but was eaten into in a remarkable manner. These strips, and particularly some of those to be described later (with peroxide of hydrogen), were not corroded most upon the edges, where one would naturally expect it, but along vertical lines running up and down the middle of the strip. In some cases they were eaten through along these lines in such a manner that nothing remained but a thin film like gold lace. It appeared that local action started in along these lines rather than at the edges, owing to differences of potential due to the distribution of the oxygen, and that when it had once set in it was able to maintain itself.

It is probable that in all cases of the solution of gold in the aerated cyanide solutions the process, as in the above case, is one of local electrolytic action, though, as it is impossible in such a case to apply the galvanometer, it would be difficult to prove this proposition except by inference.

In all such experiments it is important to be certain that the gold strips are in the same physical state, since the existence of microscopic films or unweighable traces of occluded gas cause an appreciable difference of potential in apparently similar gold strips. This is best tested by comparing the strips in the same solution. They react similarly if they are carefully cleaned with boiling acid, and are then washed with distilled water and ignited to redness side by side in the muffle or over a bunsen flame in a small porcelain dish. But if they are heated in different parts of the same bunsen flame, they frequently show quite appreciable differences of potential due to occluded gases.

The Effect of Hydrogen Peroxide.

The peroxide of hydrogen used was Marchand's medicinal, containing 3.3 per cent of available peroxide, as determined by titration with permanganate of potassium. According to the new theory, the $\text{H}_2\text{O}_2(\pm)$ takes up from the gold strip *o*, which becomes positive, two units of negative electricity and dissociates into $2(\text{OH})(-)$.

In the first experiment $\frac{M}{I}$ KCN solution containing the

usual amount of absorbed oxygen was used, and 10 cc. of this solution was placed both in B and O. Gold strips *b* and *o* were then placed in B and O, and the siphon was inserted. Both strips showed themselves of the same potential. The siphon was removed and 5 cc. of water was added to B and 5 cc. of hydrogen peroxide to O. On inserting the siphon and the electrodes, *b* proved to be electronegative, that is, the solution in B was electropositive by $+0.66$ volt; in other words, the positive current flowed through the solution from *b* to *o*.

Another experiment was made with boiled water with 0.62 per cent potassium cyanide that had been kept under $\frac{1}{8}$ inch of oil for a week. B and O were each filled with 10 cc. of this solution, and the gold strips and siphon were inserted. The strips proved to be of the same potential. The siphon was then removed, and to B was added 2 cc. of distilled water, and to O 2 cc. of hydrogen peroxide. After mixing, on replacing the siphon, the voltage rose to $+0.57$ volt. That is, the positive current flowed through the solution from *b* to *o*. To exclude the air, a layer of paraffine oil about $\frac{1}{8}$ inch thick was floated over each solution before inserting the siphon.

The resistance of 30,000 ohms was then cut out, leaving only that of the galvanometer (3,000 ohms), and the needle which had previously shown a deflection of 2.6 scale divisions was thrown out of sight. (The limits of the scale used were 21 scale divisions.) After being thus short-circuited for an hour and a half, on throwing in again the 30,000 ohms resistance, the voltage of the combination showed itself to be still in the same direction, $+0.63$ volt. The 30,000 ohms were again cut out and the combination was again short-circuited over night. In the morning some bubbles of gas from the action of the peroxide had collected in the upper part of the siphon and had nearly cut off the current. But on removing and refilling the siphon the voltage still showed itself to be in the same direction, $+0.55$ volt. The resistance of 30,000 ohms was again cut out and that of the galvanometer only left in, and after five and a half hours more the electrodes were taken out, cleaned, and weighed. Total time, twenty-three hours.

The strip contained in B had lost 13.25 milligrams, while that in O had lost only 9.20 milligrams. *Evidently, in spite of the local action that has taken place in the vessel O, more gold has dissolved in the vessel B in the absence of the oxidizing agent than in O, where the oxidizing agent was present.*

In order to determine how much of the loss in B might be due to dissolved oxygen which had leaked through, or by the oil cover into the cyanide solution since it had been made, a week previously, 10 cc. of the same solution as that used in B was placed in a similar vessel, and a gold strip was immersed in it half way, and the liquid was then covered with the paraffine oil just as had been done in B and O. After nineteen and a quarter hours it had lost 4.28 milligrams. A similar strip entirely submerged below solution and oil lost, in twenty-four hours, 2.64 milligram. These experiments prove that some air had leaked through, or by, the oil cover. It had been previously proved that if a thicker layer was used, it was possible, practically, to prevent altogether the ingress of oxygen and the solution of the gold. In this case it was inconvenient to use a layer thicker than $\frac{1}{8}$ inch. But the experiment also clearly shows that the amount of gold thus dissolved by absorbed oxygen is so much less than that shown by the *b* strip, that the solution must have been caused by the electromotive forces of the combination in the manner I have explained.

The same experiment was repeated exactly as before, except that to 10 cc. of 0.62 per cent potassium cyanide in B was added 1 cc. of water and to 10 cc. in O was added 1 cc. of peroxide of hydrogen. At first the voltage was +0.652 volt, rapidly falling to +0.63 volt. After cutting out all but 3,000 ohms resistance for twenty-one hours, the voltage, on adding the 30,000 ohms, proved to be still +0.63 volt. After again cutting out the 30,000 ohms for twenty-seven hours, it still showed, on inserting it again, +0.434, rising, after resting a few minutes, to +0.456 volt. At this point, after a total of forty-seven hours, the electrodes were cleaned and weighed, and *b* was found to have lost 24.06 milligram and *o* to have lost only 13.25 milligrams. *Here, again, the positive current has moved through the solution from b to o, and more gold*

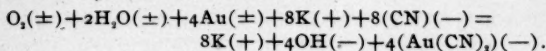
has dissolved in the vessel containing no oxidizer than in the one containing the oxidizer.

In some other experiments with peroxide of hydrogen there was more local action in *O*, and the *o* strip lost as much, and in some cases even twice as much, as the *b* strip. The exact conditions governing this local action are still under investigation. *But in these cases, also, the galvanometer showed that the positive current was still flowing through the solution from the strip b to the strip o in contact with the cyanide containing the oxidizer, and thence back through the gold strip o back again to b, the place of beginning.*

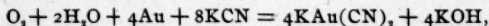
The course of the negative current may be traced from the gold strip *o* immersed in the oxygenated cyanide, to the strip *b* immersed in the unoxxygenated cyanide in two ways, as follows :

1. According to Ostwald¹ the reaction $O_2 + 2H_2O = 4OH$ produces $4 \times 21,000$ calories. Assuming this to be true, the oxygen molecule O_2 forms with the water four negative hydroxyl ions, $4(OH)(-)$; these, assuming a negative charge from the electrode *o*, cause that end of the gold electrode to be positively electrified. Now these negative ions travel through the solution, displacing at the other end of the line four negatively electrified cyanogen ions, $4(CN)(-)$, which give up their negative charge at the other gold electrode *b*, and thus enable four positive gold ions, $4Au(+)$, to go into solution there, forming with eight cyanogen ions four complex negative ions, $4(Au(CN)_2)(-)$.

The water present may be regarded as not dissociated appreciably, and the dilute solution of cyanide of potassium as entirely so. Making these assumptions, the principal reactions may be expressed as follows :



But this is equivalent to the so-called Ellsner reaction :

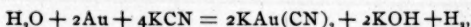


which Maclaurin² has proved to be quantitatively correct.

¹ "Chemische Energie," p. 956.

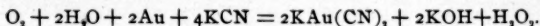
² J. Chem. Soc., 63, 728.

2. The other view, following Traube, has been urged by Bodlaender, of the Clausthal *Bergakademie*.¹ He shows first, in agreement with Maclaurin and myself, that the reaction



proposed by Macarthur to explain the solution of cyanide of gold in cyanide solutions, is incorrect. Next, he claims that the so-called Ellsner reaction really proceeds in two stages:

(a) The hydrogen, which is not formed according to Macarthur's reaction, is, in the presence of cyanide of potassium, water, gold, and oxygen, potentially nascent; and a molecule of oxygen combines directly with 2 atoms of nascent hydrogen, forming hydrogen peroxide, while 2 atoms of gold dissolve; thus:



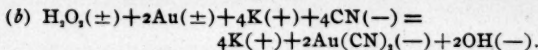
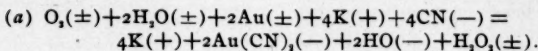
(b) Next, the hydrogen peroxide gradually dissociates into hydroxyl, and causes the solution of two more atoms of gold, thus:



The sum of these two reactions is, of course, the same as that of the Ellsner reaction, which correctly expresses the end result.

When gold was rapidly dissolved in an aerated cyanide solution, Bodlaender was able to detect as much as 72.3 per cent of the hydrogen peroxide required by reaction (a); and, as reaction (b) had probably already set in, this renders this explanation extremely probable.

Expressed in terms of the ions, reactions (a) and (b) become:



The flow of ions through the solution is the same as in the first case. On the whole, the second seems the more proba-

¹ *Ztschr. angew. Chem.*, 1896, 583.

ble explanation, though either agrees with most of the facts.¹

According to either of these views the new theory agrees quantitatively with the results of experiment, but offers for the first time a consistent explanation of its occurrence. *It is due to the superior electromotive force of the oxygen, or, in case they are present, to some other electronegative ions, as $(OH)(-)$, $Cl(-)$, $Br(-)$, etc., together with the capacity of the gold for forming complex ions with cyanogen.*

If, instead of having the two ends of the gold strip immersed in two separate cyanide solutions, the strip is immersed in the same solution containing some dissolved oxy-

¹ While this paper was in press, a paper on "Freiwillige Oxydation" (Auto-oxidation), by Dr. Manchot, of Goettingen, has appeared, in which he has examined the oxidation of a large number of phenol derivatives, such as those used as developers in photography. One of these derivatives, oxanthranol, was particularly well adapted to give quantitative results, and he was able to prove that for every molecule of oxygen absorbed a molecule of hydrogen in the oxanthranol was oxidized, and a molecule of hydrogen peroxide was formed.

Representing the organic radical by R, and the oxanthranol by RH_2 , he assumes that the reaction takes place as follows:



The organic radical, if unstable, is frequently still further oxidized in a second reaction by the hydrogen peroxide thus formed.

It would appear that similar reactions ensue in the rusting of metals in damp air. The rusting of iron, zinc, etc., is worthy of thorough study in the light of the new ideas.

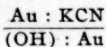
It would seem that the modern electrochemical views necessitate a return, in part at least, to the ideas of Berzelius and Schoenbein. They supposed that the same element was at times positively, and at other times negatively, electrified. This appears to be a consequence of the new view also. For if we regard the oxygen molecule $O_2(\pm)$ as electrically neutral, this can only be the case when one of its atoms has a double positive and the other an equal negative charge. By the attraction of these charges the molecule may be regarded as being held together. Its real composition then would be $O(-) + O(+)$. On the other hand, two atoms of oxygen in the elemental state would be similarly electrified with negative electricity, thus: $O(-)$, $O(-)$, and would consequently repel each other. Hence, to change an oxygen molecule into two oxygen atoms would require four units of negative electricity.

On the other hand, the hydrogen molecule would be composed as follows: $H(+)+H(-)$; and to change it into two hydrogen atoms $H(+)$ and $H(-)$ would require two units of positive electricity.

It would also seem necessary to assume that there is an inherent tendency in the oxygen molecule (due, perhaps, to some peculiarity of shape or volume) to assume negative, and in the hydrogen molecule to assume positive electricity in dissociating.

It would also appear as if a different result ought to be produced when neutral hydrogen molecules combine with a neutral oxygen molecule, from that which results from the combination of positively electrified hydrogen atoms with a neutral oxygen molecule. This may be the key to the formation of water in the one case and hydrogen peroxide in the other.

gen, the same electrolytic action can still go on as a case for "local action" for the couple



is still possible if we regard the gold to be short-circuited on itself, and the explanation given above still applies.

When I began this investigation, in 1896, I marked out for myself a much wider range of investigation than here outlined, and the course of its partial execution has suggested many other interesting questions, some of which are still under investigation, but the constant and pressing interruptions of routine work have made it impossible to carry the work further at the present time.

IV. Conclusions.

Whatever may be the nature of the objections that may be raised against the final acceptance of the modern electrolytic theory in its present form, it will, I think, be conceded that the following conclusions may be fairly drawn from the foregoing :

1. That the new electrolytic theory explains in a remarkably complete manner the reason for the departure of metals immersed in cyanide solutions from the sequence of electromotive force which they present in acid solutions.
2. That it is the only theory ever presented that gives any clue to the remarkable aberration of cyanide solutions from all the usual chemical analogies.
3. That it explains in an entirely adequate manner the reason for the reactions that go on when gold, silver, and other metals are dissolved and precipitated from cyanide solutions.
4. That the determination of the electromotive force of the metals in cyanide solutions, under different conditions, offers a means of research that is likely to be of great practical utility in determining the direction and intensity of chemical reactions, under fixed conditions, or in following them under changing conditions, just as they occur.
5. That the differences of electromotive force of metals in dilute cyanide solutions do not give much support to the so-

called "selective affinity of dilute cyanide solutions for gold," the only common metal that shows any indication of such favorable action being copper.

6. It is probable that, in the absence of external electromotive forces, an aerated cyanide solution less than $\frac{M}{10,000}$, or 0.00065 per cent, is without action on metallic gold.

7. That for all practical purposes, an aerated cyanide solution of less than 0.001 per cent, is without action on metallic gold.

This study has led apparently far afield from the practical side of the cyanide process; yet I hope that it may be of service in at least calling attention to the work of others who have toiled for many years in attempting to clear up some of the most subtle questions that have ever taxed the human mind, for I am firmly convinced that, in the long run, such work is always of the greatest practical service. In these days, the words of Ostwald have certainly come true:

"The science of to-day is the practice of to-morrow."

REVIEWS.

THE EXPERIMENTAL STUDY OF GASES. An account of the experimental methods involved in the determination of the properties of gases and of the more important researches connected with the subject. By MORRIS W. TRAVERS, D.Sc. Macmillan & Co. 1901.

We are but just beginning to realize the existence of matter devoid of chemical properties, which seems to have been predestined from the beginning of things never to enter into combination. These elements, for elements they seem to be, which went into the "discard," so to speak, during the process of cosmical evolution, have either remained free in the earth's atmosphere, or else have been locked up as mechanical inclusions in certain minerals.

Those which have been discovered up to the present time are all gaseous, but there seems to be no reason why we may not suspect the existence of inert substances which are either solid or liquid under ordinary conditions. Possibly the minute traces of insoluble residue which are left over in certain mineral analyses, and described as "probably silicon" or "doubtless rhodium" will bear looking into. It was the small insoluble residue in a certain gas reaction that furnished the

first clue to the existence of this interesting class of elements.

The separation and purification of substances of this nature must clearly be accomplished by physical means, and the two physical processes generally made use of for the separation of dissimilar substances, are crystallization and fractional distillation. Fortunately the great advances which have been made during the last ten years in the methods of getting extremely low temperatures, make the application to gases of the process of fractional distillation, and even crystallization, almost as simple as it is in the case of liquids. Mr. Travers has given us a very satisfactory handbook on the subject of the experimental study of gases, which will be found extremely useful to every chemist and physicist. It is profusely illustrated, and an unusually large amount of space is given to manipulation, a circumstance which will make every experimenter grateful to the author.

Nearly 100 pages, at the start, are devoted to mercury pumps, stop-cocks, various forms of apparatus used in storing, transferring and measuring gases, methods of preparing pure gases, and the devices necessary to the handling of small amounts of rare gases to the best advantage.

The chapter on the measurement of volume, and the one following it on gas analysis, will be found of especial interest to chemists. The author recommends the use of the siphon burette unless a large number of analyses are to be made. With this piece of apparatus, which any one with a rudimentary knowledge of glass-blowing can construct for himself, the complete analysis can be made, the reagents being kept in ordinary bottles instead of in the somewhat complicated pipettes described by Hempel and others. The method seems to be especially adapted to laboratories provided with a limited equipment.

In brief, it consists in the introduction into a tube filled with mercury and inverted over a jar of the same fluid, of a small quantity of the gas-absorbing reagent. The gas is then allowed to bubble up into the tube from the graduated siphon burette. After the absorption the residue is drawn back into the pipette and its volume recorded. The same process is then repeated with the other reagents, the final explosion being made in the same instrument by means of eudiometer electrodes sealed into the top of the graduated tube. The simplicity of the method is its strong recommendation, although, as the author says, the Oettel pipettes will probably be found more convenient in the case of commercial analyses.

Following this we have an interesting account of the inert gases helium, argon, néon, krypton, and xenon, and the

methods by which they were isolated. This subject is treated very explicitly; if the experimenter wishes to collect a small amount of argon to fill a vacuum-tube, or prepare a large quantity for the investigation of its physical properties, the best method for each case is given.

The author next takes up the determination of gas density and the relations between temperature pressure and volume. Following this comes the subject of the liquefaction of gases, in which the developments are traced from Faraday's bent tube to the regenerative machines of Linde and Hampson for the liquefaction of air. This chapter concludes with a very complete description of the apparatus used by the author for the liquefaction of hydrogen, and of the precautions which must be taken in its use. A chapter follows on the manipulation of liquid gases, their fractional distillation, and their use in the maintaining of constant low temperatures.

The author throws out frequent suggestions to those engaged upon research work, pointing out many of the gaps in our knowledge which require filling, such, for example, as the effect of pressure on the composition of the distillate passing over at a definite temperature. This question has been investigated in the case of water and certain organic fluids, but practically nothing is known of the behavior of mixtures of liquefied gases. This is a question of vital importance in the separation of gases by physical processes.

The last part of the book is devoted to the determinations of vapor-pressure and the critical constants, the specific heat of gases, and the phenomena of effusion, transpiration, and diffusion, the closing chapter dealing with the subject of spectrum analysis, with instructions for the construction, filling, and use of vacuum tubes, which will be found helpful. If one has but a cubic centimeter of a pure gas and will fill a vacuum tube with it and then recover all but the minute trace left in the exhausted tube, without contaminating it with impurities in the meantime, it is important to know beforehand exactly how to proceed, and exactly what precautions to take.

The book contains a vast amount of information and is admirably adapted to the requirements of students, both as a text-book and as a guide to work in the laboratory whether elementary or advanced.

Sufficient space is given to theory and experiment to make it interesting reading, while the very large amount of information regarding manipulation makes it invaluable in the laboratory as a reference book.

Mention should be made too of the admirably executed diagrams. We none of us ever quite get over the early contracted

habit of liking to look at the pictures, and the pictures in Mr. Travers' book certainly invite the reader to take up the study of gases for the mere pleasure of making and using the apparatus, if for nothing else.

R. W. WOOD.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By HARRY C. JONES. New York: The Macmillan Company. 1902. pp. 565 + vii. Price, \$4.00.

The following extracts from the preface of this book will serve to introduce it to chemists:

"It has been the aim of the author to deal with the whole subject of physical chemistry in an elementary manner. The rapidly increasing desire, on the part of students of chemistry and physics, to know more of physical chemistry is manifesting itself in every direction. It is with the object of helping such students in the later stages of their college work and in the earlier part of their university career that this work has been prepared."

"In reference to the contents of that portion of the work which deals with the newer physical chemistry, a few words should be added in this connection. The new physical chemistry really begins with the chapter on solutions, and this is one of the most important chapters. The discovery of the relations between dilute solutions and gases has placed the subject of solutions at the very foundations of the new developments in physical chemistry."

"Electrochemistry, on the other hand, is of the very greatest importance. In no chapter of physical chemistry have greater advances been made in recent time, and nowhere do we find experimental work of greater value.

"The study of chemical dynamics and statistics has been very much to the front ever since the recognition of the importance of the law of mass action. It will be observed that reaction velocities and equilibrium in chemical reactions have been dealt with from the standpoint of this law. This appeals to the author as being the most exact and by far the simplest method of treating these problems. The phase rule, however, is considered at sufficient length, and applied, it is hoped, to a sufficient number of cases to make clear this important generalization.

"An attempt has been made to prepare a balanced work. The danger of treating certain subjects too fully and of following certain deductions beyond the scope of the remainder of the book has been felt, and an earnest endeavor has been made to avoid this defect."

"Little need be said at this date in reference to the importance of the whole subject of physical chemistry. It has already extended into nearly every field of chemical science,

contributing largely to the interpretation of phenomena hitherto not understood. It has thrown light on so many problems in chemistry that it has now become an integral part of that science. And it is recognized that no chemist to-day, scientific or technical, can omit physical chemistry without losing an essential part of his training."

SAMMLUNG CHEMISCHER UND CHEMISCH-TECHNISCHER VORTRÄGE. Herausgegeben von PROFESSOR DR. FELIX B. AHRENS. VI Band; 12 Heft. Ueber feste Lösungen, von Dr. Guiseppe Bruni, Privatdozent an der Universität Bologna. Deutsch von Dr. E. E. Basch, Wien. Mit 4 Abbildungen. 1901. pp. 55. Verlag von Ferdinand Enke, Stuttgart.

This monograph begins with a discussion of the origin of the conception of solid solutions, and then takes up the methods by which solid solutions can be formed. A very brief section is devoted to the state of molecular aggregation of substances in the solid condition, and the phase rule is then applied at length to the subject of solid solutions.

The second portion of the monograph is devoted to the relations between the chemical constitution of substances which can form solid solutions with one another. This comprises both inorganic and organic compounds, and discusses the beautiful investigations of Piccini, Garelli, Ciamician, Ferratini, and others.

It is to be regretted that one of the most important investigations on solid solutions has not found its way into this monograph. Küster has shown how it is possible to determine the molecular weights of pure solids by means of solid solutions, and has furnished us with the only method available for determining the molecular weights of solids. This is indeed the most important scientific application of the ideas worked out by van 't Hoff concerning the existence and nature of solid solutions.

The author has increased the value of his work by giving reference to the literature of his subject. H. C. J.

PHYSIKALISCHE CHEMIE FÜR ANFÄNGER. VON DR. CH. M. VAN DEVENTER. Mit einem Vorwort von PROF. DR. J. H. VAN 'T HOFF. Zweite Auflage, besorgt von DR. ERNST COHEN. Amsterdam: S. L. Van Looy; Leipzig: Wilhelm Engelmann. 1901. pp. 168.

The appearance of the first edition of this book has already been noticed in this Journal. (Vol. 19, 916.) The translation into English was subsequently reviewed (Vol. 21, 277), and it now only remains to call attention to the fact that the second German edition has appeared. H. C. J.